

TERMODYNAMISKA UNDERSÖKNINGAR
AV KOMPLEXBILDNINGSREAKTIONER
I LANTANOID- OCH SKANDIUM-
DIKARBOXYLATSYSTEM

av

Göran Gårdhammar

Lund 1972
— —

TERMODYNAMISKA UNDERSÖKNINGAR
AV KOMPLEXBILDNINGSPREKTIONER
I LANTANOID- OCH SKANDIUM-
DIKARBOXYLATSISTEM

AVHANDLING FÖR FILOSOFIE DOKTORSEXAMEN

Avhandlingen kommer att försvaras vid offentlig disputation
å Kemicentrum, hörsal C, tisdagen den 23 maj 1972 kl 10.15.

av

Göran Gårdhammar

Fil lic, MIm



Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41545326_0019

TERMODYNAMISKA UNDERSÖKNINGAR
AV KOMPLEXBILDNINGSPREKTIONER
I LANTANOID- OCH SKANDIUM-
DIKARBOXYLATSISTEM

av

Göran Gårdhammar

Lund 1972

UNIVERSITY OF LEIDEN
LIBRARY
DEPARTMENT OF THE HISTORY OF SCIENCE
AND TECHNOLOGY

UNIVERSITY OF LEIDEN



UNIVERSITY OF LEIDEN

Avhandlingen är en sammanfattning av följande fem uppsatser, vilka samtliga ingår i serien "Thermodynamic Properties of Rare Earth Complexes":

- A. Grenthe, I., Gårdhammar, G. and Rundcrantz, E. VI. Stability Constants for the Oxalate Complexes of Ce(III), Eu(III), Tb(III) and Lu(III). Acta Chem. Scand. 23 (1969) 93.
- B. Gårdhammar, G. VIII. Stability Constants for Oxalate Complexes of Sc(III). Acta Chem. Scand. 25 (1971) 158.
- C. Grenthe, I. and Gårdhammar, G. X. Complex Formation in Aqueous Solution of Eu(III) and Iminodiacetic Acid. Acta Chem. Scand. 25 (1971) 1401.
- D. Grenthe, I. and Gårdhammar, G. XIII. Free Energy, Enthalpy and Entropy Changes for the Formation of Rare Earth(III)-Iminodiacetate Complexes. Under tryckning i Acta Chem. Scand.
- E. Gårdhammar, G. XV. Free Energy, Enthalpy and Entropy Changes for the Formation of Rare Earth(III)-Ethylenediamine-N,N'-diacetate Complexes. Skall publiceras i Acta Chem. Scand.

INNEHÅLLSFÖRTECKNING

INLEDNING	1
BETECKNINGAR	7
EXPERIMENTELLA DETALJER OCH TOLKNING AV MÄTDATA	8
Jonmedium och temperatur	8
Översikt av olika komplexbildningsreaktioner	8
Inledande beskrivning av potentialmätningarna	11
Eu-IMDA-systemet (Potentiometri)	13
Övriga IMDA-system (Potentiometri)	17
EDDA-systemen (Potentiometri)	17
Ce-oxalatsystemet	18
Sc-oxalatsystemet	20
Slutkommentar angående existensen av $M_{PQR}H_A$ -komplex	22
Kalorimetriska mätningar	23
Jämförelser med tidigare undersökningar	26
AVSLUTANDE DISKUSSION	32
Koordinationssättet för de olika metallkomplexen	32
Donatoregenskaper hos olika atomer	34
Effekten av olika atomantal i kelatringen	35
Variationen av termodynamiska storheter genom lantanoidserien	37
Maximalt koordinationsstal och steriska hinder	38
REFERENSER	41
APPENDIX: Ref. A-E.	

TABELL- OCH FIGURÖVERSIKT

<u>Tabell 1.</u> Sammanfattning av undersökningar, som författaren har utfört.	3
<u>Tabell 2.</u> Effektiva jonradier i Å för de sällsynta jordartsmetallernas 3-värda joner.	5
<u>Tabell 3.</u> Stegvisa komplexbildningskonstanter m m.	16
<u>Tabell 4.</u> Jämförelser mellan protonupptagningen $\text{Ligand} + \text{H}^+$ och komplexbildningsreaktionen $\text{Ligand} + \text{M}^{3+}$.	24
<u>Tabell 5.</u> Termodynamiska storheter för IMDA-systemen.	27
<u>Tabell 6.</u> Termodynamiska storheter för EDDA-systemen.	28
<u>Tabell 7.</u> Översikt av olika författares EDDA-studier.	29
<u>Tabell 8.</u> Jämviktskonstanter för oxalatsystem, bestämda av T. Sekine.	31
<u>Tabell 9.</u> Jämförelser mellan termodynamiska storheter från dipikolinat- och IMDA-system.	36
<u>Figur 1.</u> Formler för olika karboxylatjoner.	2
<u>Figur 2.</u> Species som dominerar i proton-IMDA- och proton-EDDA-systemen.	10
<u>Figur 3.</u> Sannolika koordinationssätt för komplexen MA^+ och MHA^{2+}	33

INLEDNING

Under de senaste två decennierna har komplexföreningar med trevärda joner av de sällsynta jordartsmetallerna (Sc, Y, La-Lu) studerats vid avdelningarna för oorganisk och fysikalisk kemi i Lund. Dessa arbeten omfattar:

I) Termodynamiska undersökningar av komplexbildningsreaktioner i lösning genom bestämningar av jämviktskonstanter med olika metoder samt kalorimetriska bestämningar av förändringar i entalpi och värmekapacitet. (Referenser: A-E och 1-18.)

II) Kinetiska studier av olika komplexsystem.^{19,20}

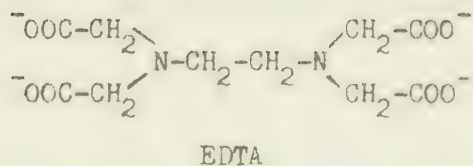
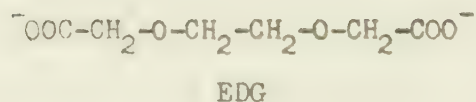
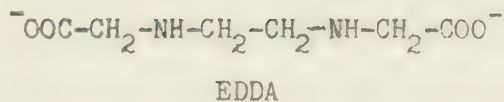
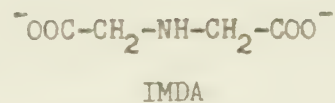
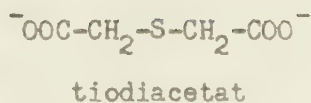
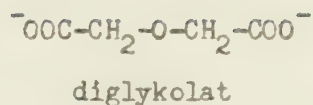
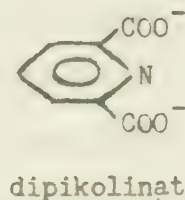
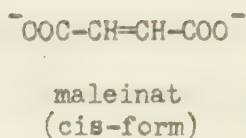
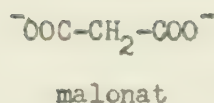
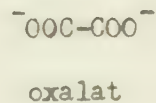
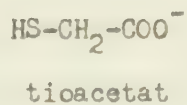
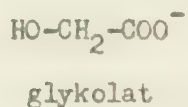
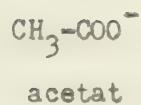
III) Röntgenkristallografiska undersökningar av komplex i fast fas.^{21,22}

De flesta liganderna är olika dikarboxylat: Oxalat, malonat, maleinat, diglykolat, dipikolinat, tiodiacetat, iminodiacetat (IMDA), etylendiamin-N,N'-diacetat (EDDA) och etylendiglykolat (EDG). Andra ligander, som studerats, är acetat, glykolat, tioacetat och EDTA. (Formlerna för dessa 13 joner återfinnes i fig. 1.)

De undersökningar, som författaren har utfört, tillhör alla grupp I enligt ovan. Tabell 1 ger en översikt av vilka komplexsystem som behandlas i ref. A-E. För samtliga ligander har jämviktskonstanter bestämts. I en del fall har även kalorimetriska mätningar gjorts varvid entalpi- och entropidata har kunnat erhållas. De olika mätmetoderna är också angivna i tabellen.

De sällsynta jordartsmetallernas trevärda joner är typiska A-acceptorer,²³ dvs de koordinerar bäst med starkt elektronegativa donatoratomer som fluor, syre och kväve. Ligandfältseffekter

Figur 1. Formler för olika karboxylatjoner. Acetat, glykolat och tioacetat har laddningen -1. Laddningen för EDTA är -4. Övriga joner är av typ di-karboxylat med laddningen -2.



Tabell 1. Sammanfattning av undersökningar, som författaren har utfört.^{x)} De tre första metoderna avser bestämningar av jämviktskonstanter. Pot. = Potentiometri. Lösl. = Löslighetsmätningar. Extr. = Extraktionsmätningar. Kal. = Kalorimetri.

Ligand	3-värda metalljoner (Laddn. utelämnad)	Pot.	Lösl.	Extr.	Kal.	Ref.
Oxalat	Ce					A ^{x)}
"	Sc					B
IMDA	Pr, Eu, Ho, Lu					C, D
"	Sc					D
EDDA	La, Nd, Sm, Tb, Er, Yb					E
"	Gd, Dy					E

^{x)} I ref. A ingår också undersökningar av Eu-, Tb- och Lu-oxalat-systemen, utförda av I. Grenthe och E. Rundcrantz.

påverkar endast mycket obetydligt termodynamiska data eftersom 4f-elektronerna hos jonerna Ce^{3+} - Lu^{3+} är effektivt skärmade av elektroner i 5s- och 5p-orbitalerna. Jonerna Sc^{3+} , Y^{3+} och La^{3+} har ädelgaskonfiguration. Starka komplex i vattenlösning fås nästan enbart med flertandade ligander.^{24,25} Den ökande effektiva kärnladdningen i lantanoidserien medför att jonradien minskar succesivt från La^{3+} till Lu^{3+} . Y^{3+} är ungefär lika stor som Ho^{3+} medan Sc^{3+} är avsevärt mindre än Lu^{3+} ; jonernas radier återfinnes i tabell 2. Jonstorleken är av fundamental betydelse för speciellt hydrataion, koordinationsstal och koordinationsgeometri.

Strukturundersökningar av fasta faser har visat att det normala koordinationsstalet för lantanoidjonerna oftast är 6-9, någon gång t o m 12.^{21,26-29} Sc har sannolikt i de flesta fall ett koordinationsstal på 6-8.^{21,30-32} Koordinationspolyedern omkring metalljonen utgörs ofta av ett kvadratisk antiprisma (8-koordinat), en dodekaeder (8-koord.) eller ett distorderat trigonalt prisma med ytterligare två eller tre koordinerade atomer i ekvatorialplanet (8- och 9-koord.).

Resultaten av egna och andras lösningskemiska arbeten samt strukturundersökningar av analoga komplex i fast fas har använts för att belysa följande problemställningar:

a) Jämviktskonstantens storlek kan ofta ge en antydning om hur liganden är bunden i komplexet. Ett högt värde på denna konstant gör kelatbildning (med ett eller flera ringsystem) sannolikt. Sura komplex kan bildas; även för dessa är ett flertal koordinationsstätt möjliga.

Tabell 2. Effektiva jonradier i Å för de sällsynta jordartsmetallernas 3-värda joner. Värdena är korrelerade till radien för 6-koordinerat O^{2-} , som har satts = 1.40 Å. (Efter Shannon and Prewitt, Acta Cryst. B25 (1968) 925.)

Koordinations- tal Jon	6	7	8	9	10	12
La ³⁺	1.061	1.10	1.18	1.20(?)	1.28	1.32(?)
Ce ³⁺	1.034		1.14			1.29
Pr ³⁺	1.013		1.14			
Nd ³⁺	0.995		1.12	1.09(?)		
Pm ³⁺	0.979					
Sm ³⁺	0.964		1.09			
Eu ³⁺	0.950		1.07			
Gd ³⁺	0.938		1.06			
Tb ³⁺	0.925		1.04			
Dy ³⁺	0.908		1.03			
Ho ³⁺	0.894		1.02			
Er ³⁺	0.881		1.00			
Tm ³⁺	0.869		0.99			
Yb ³⁺	0.858		0.98			
Lu ³⁺	0.848		0.97			
Sc ³⁺	0.730		0.87			
Y ³⁺	0.892		1.015			

b) Liganderna diglykolat, tiodiacetat, iminodiacetat och dipikolinat är geometriskt likartade. Skillnader i komplexens styrka bör då kunna relateras till olikheter i donatoregenskaperna för syre, svavel, iminokväve och pyridinkväve. Liknande jämförelser kan också göras mellan EDDA och EDG.

c) Jonerna oxalat, malonat och maleinat ger analoga kelatkomplex. Man får här en möjlighet att studera hur den relativa stabiliteten hos komplex av samma typ och med samma antal donatoratomer beror på kelatringens storlek.

d) Variationen av de olika termodynamiska storheterna genom lantanoidserien är för många ligander, t ex diglykolat och dipikolinat, tämligen likartad.^{5,7} Detta antyder att centraljonens hydrata-tion spelar en avgörande roll vid komplexbildningen. För att ytterligare kunna utveckla denna teori är det värdefullt om fler ligander undersöks. IMDA ingår i en serie av geometriskt likartade ligander, jfr punkt b. EDDA och den analoga jonen EDG är exempel på fyrtandade ligander med likartad geometri.

e) Koordinationstalet för de olika komplexsystemen kan uppskattas med hjälp av det maximala antalet ligander som komplexbindes. Detta koordinations-tal kan jämföras med motsvarande värde som erhålles vid röntgenkristallografiska undersökningar av samma komplex i fast fas.

f) Kvoterna mellan jämviktskonstanterna för de olika komplexbildningsstegen ger en antydning om eventuella geometriska hinder för ligandernas koordination. För exempelvis diglykolat och dipikolinat har man tidigare diskuterat dessa problem.^{5,7,10} Dylika steriska hinder, orsakade av ligand-ligandrepulsion, accentueras givetvis när donatoratomernas antal ökar och liganden blir större och alltmer komplicerat uppbyggd. - Jämförelser med fasta-fasundersökningar är även i detta fall aktuella.

BETECKNINGAR

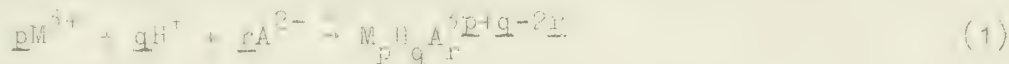
M = sällsynt jordartsmetall, dvs Sc, Y eller någon av lantanoiderna (La - Lu).

$H_N A$ = karboxylsyra. Oxalat, IMDA och EDDA betecknas A^{2-} . (I forts. sättes $N=2$, dvs de nedan angivna laddningarna skall ändras när $N \neq 2$.)

C_M, C_H, C_A = totalkoncentration av respektive metall, fria och dissocierbara vätejoner samt karboxylat.

$\underline{m}, \underline{h}, \underline{a}$ = $[M^{3+}], [H^+], [A^{2-}]$ = koncentration av respektive fri metalljon, vätejon och karboxylatjon.

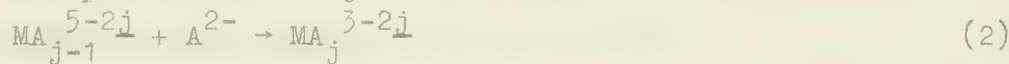
β_{pqr} = jämviktskonstant för reaktionen



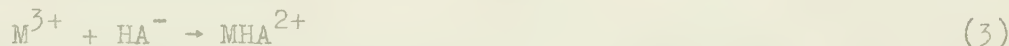
$\Delta G_{pqr}^0, \Delta H_{pqr}^0, \Delta S_{pqr}^0$ = förändringar i fri energi, entalpi och entropi för bildning av en mol komplex enl reaktion (1).

$\beta_{\underline{j}} = \beta_{\underline{r}} = \beta_{10\underline{r}}$ ($\beta_0 = 1$)

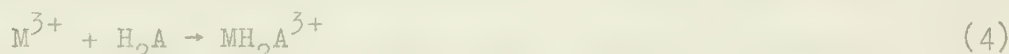
$K_{\underline{j}}$ = stegvis komplexkonstant = jämviktskonstant för reaktionen



K_M, K_{M2} = jämviktskonstanter för reaktionerna



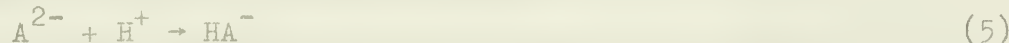
och



$\Delta G^0, \Delta H^0, \Delta S^0$ med index $\underline{j}$, M eller M2 motsvarar förändringar i fri energi, entalpi och entropi för resp reaktion (2), (3) och (4).

$\delta_{\underline{j}} = \delta_{\underline{q}}$ = protoneringskonstant = $\beta_{0\underline{q}1}$

K_S, K_{S2} = jämviktskonstanter för reaktionerna



och



$\bar{n}$ = (totalkonc. komplexbunden ligand)/ C_M

$\alpha_{pqr} = p[M_p H_q A_r^{3p+q-2r}]/C_M$

$\underline{X} = \sum_{\underline{j}=0}^J \beta_{\underline{j}} \cdot \underline{a}^{\underline{j}}$ (De komplex som bildas är $MA, MA_2 \dots MA_J$)

EXPERIMENTELLA DETALJER OCH TOLKNING AV MÄTDATA

Jonmedium och temperatur

Den formella jonstyrkan har varit 1.00 M i samtliga fall utom vid löslighetsmätningarna då $[\text{Na}^+]$ har varit 1.00 M. Som neutralsalt har NaClO_4 genomgående använts.

Oxalatsystemen undersöktes vid 20 °C, de andra systemen vid 25 °C. Valet av den lägre temperaturen i det första fallet beror på att löslighetsmätningar har använts. Det är då oftast en fördel om man efter jämviktsinställningen slipper sänka temperaturen när den fränfiltrerade lösningen skall analyseras. (Rumstemperaturen var ca 22 °C.)

Översikt av olika komplexbildningsreaktioner.

Samtliga använda ligander (oxalat, IMDA och EDDA) är dikarboxylatjoner. Den stökiometriska sammansättningen $\text{M}_p\text{H}_q\text{A}_r$ $^{3p+q-2r}$ av de dominerande komplexen brukar oftast bestämmas genom mätningar där storheterna $\underline{C}_M$, $\underline{C}_H$ och $\underline{C}_A$ systematiskt varieras. Variationsområdets storlek för dessa halter bestämmas bl a av nödvändigheten att hålla jonmediet någorlunda konstant. I en del fall medger dessutom den experimentella metoden ej någon oberoende variation av vissa storheter.

När man gör den första ansatsen att tolka mätdata antar man ofta att det endast bildas "normala" komplex för vilka $p = 1$ och $q = 0$.^{24,25} I de aktuella systemen bör flerkärniga komplex, $p > 1$, ej spela någon betydelsefull roll eftersom $\underline{C}_M$ -värdena är förhållandevis små. Hydrolyskonstanterna³³⁻³⁶

indikerar att hydroxokomplex, $q < 0$, bör vara försumbara eftersom $MA_{\underline{r}}^{3-2r}$ -komplexen säkerligen är ganska starka.^{24,25} Sura komplex, $q > 0$, är däremot mer sannolika. Jonerna A^{2-} är flervärda baser och man måste beakta möjligheten av komplexbildning med ligander av typen $H_q A^{q-2}$, $q \geq 1$.

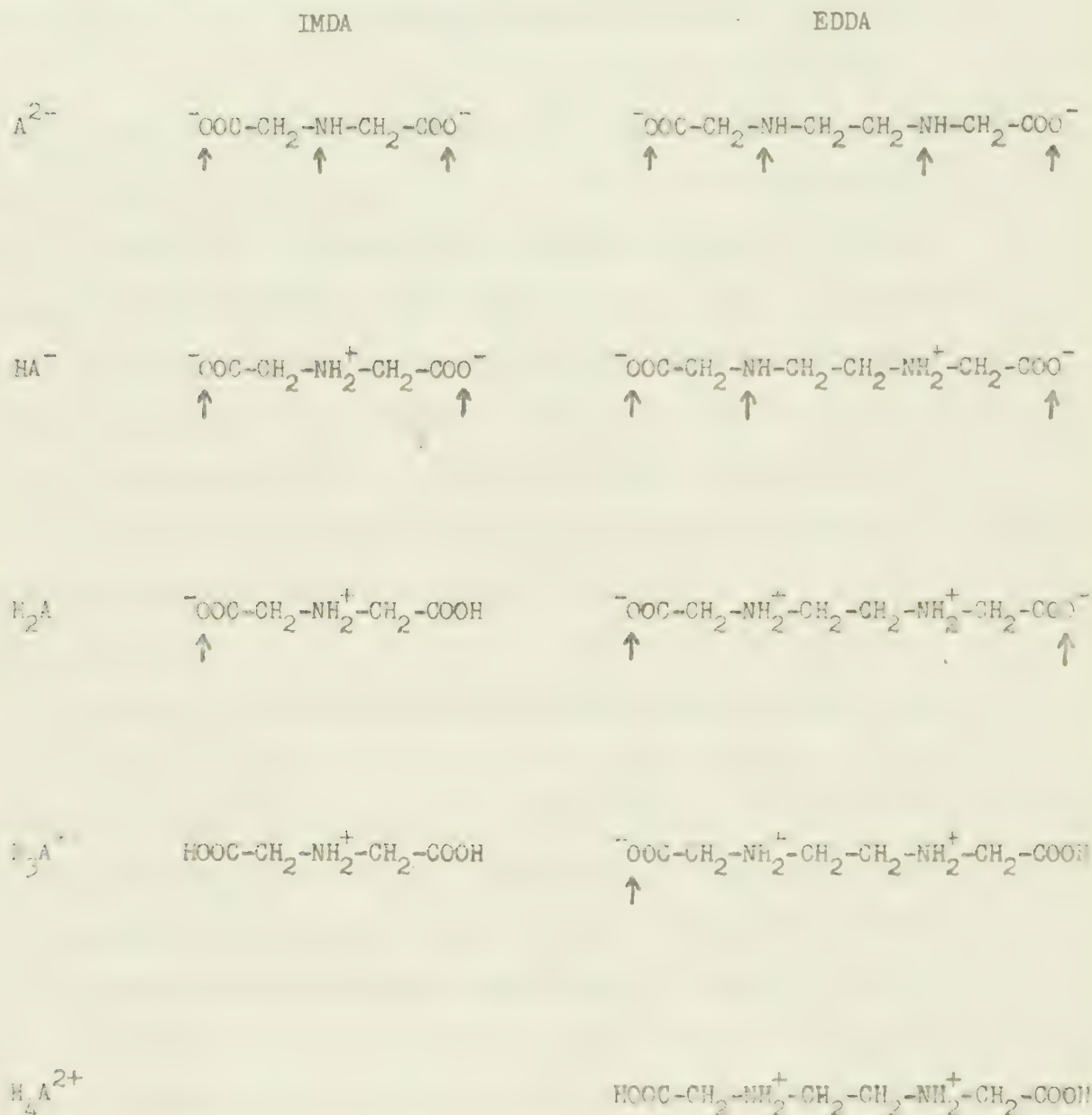
I oxalatsystemet är jonen HA^- en potentiell komplexbildare eftersom en av de två karboxylatgrupperna fortfarande är tillgänglig för koordination. Oxalatjonen, A^{2-} , har dock så pass svag basicitet att sura komplex av typen MHA^{2+} sannolikt inte spelar någon betydelsefull roll. Detta resonemang utvecklas längre fram i texten, jfr s. 23. Oxalsyra, H_2A , är rimligtvis en svag komplexbildare eftersom den är en oladdad molekyl, som saknar atomer med negativa överskottsladdningar.

I IMDA- och EDDA-systemen kan - jämfört med oxalatsystemet - en respektive två extra protoner bindas tack vare iminogruppernas relativt starka basicitet. Därvid erhålles jonerna H_3A^+ resp. H_4A^{2+} . Strukturformler för de olika species som med all säkerhet dominerar i respektive protonsystem visas i figur 2. Väteatomernas placeringar i proton-IMDA-systemet kan indikeras genom IR-studier (ref. C, s. 1405), genom strukturundersökningar av fasta faser²² och genom entalpibestämningar för reaktionerna $H^+ + H_{q-1}A^{q-3} \rightarrow H_q A^{q-2}$; $q \geq 1$ (tab. 5 i ref. D). Strukturerna för proton-EDDA-species bör vara analoga med motsvarande IMDA-species. Entalpidata stöder detta antagande. (Jfr tab. 6 i ref. E.)

I både IMDA- och EDDA-systemen har A^{2-} stark basicitet. Sura komplex bör således vara relativt sannolika i dessa fall. Denna förmodan styrks av röntgenkristallografiska undersökningar. (Ref. 22 och ref. C, s. 1401.) De olika ligander, som är tänkbara i IMDA-system, är A^{2-} , HA^- och H_2A . (Jämför figur 2). I EDDA-systemen

Figur 2. Species som dominerar i proton-IMDA- och proton-EDDA-systemen.

Tänkbara donatoratomer vid koordination är utmärkta med $\uparrow$.



kan species av typ $H A_{\underline{q}}^{q-2}$ med $\underline{q} = 0-3$ fungera som komplexbildare. (Se fig. 2.)

Sammanfattning. För oxalatsystemen kan man till en början förutsätta att endast normala komplex ($MA_{\underline{r}}^{3-2\underline{r}}$) bildas. I IMDA- och EDDA-systemen finns däremot troligen sura komplex närvarande i förhållandevis stora mängder. De metallkomplex, som främst bör vara aktuella här, är således $MH A_{\underline{q}}^{3+q-2\underline{r}}$ -species med $\underline{q} \leq 0$ och $\underline{r} > 1$.

Vid tidigare gjorda undersökningar av motsvarande komplexsystem har - med något undantag³⁷ - endast normala komplex medtagits.

Inledande beskrivning av potentialmätningarna.

Någon form av potentiometrisk titrering brukar oftast vara att föredraga vid studier av komplexjämvikter. (Jfr nedan.) Varken den fria metall- eller dikarboxylathalten ($\underline{m}$ resp. $\underline{a}$) har emellertid kunnat erhållas som primärdata eftersom inga lämpliga elektroder var tillgängliga för detta ändamål när mätningarna skulle utföras. (Under senare år har dock en oxalat-reversibel elektrod beskrivits.³⁸) Eftersom samtliga joner A^{2-} är korresponderande baser till svaga syror kan i princip komplexbildningens förlopp studeras genom mätning av vätejonkoncentrationen. Denna metod har använts för IMDA- och EDDA-systemen samt delvis vid undersökningarna av Sc-oxalatsystemet. Experimentella detaljer återfinnes i ref. B och C.

Den potentiometriska metoden är, jämförd med de andra metoder, som har använts, relativt noggrann, enkel och snabb. En fördel är dessutom att man kan variera storheterna $\underline{C}_M$, $\underline{C}_H$ och $\underline{C}_A$ oberoende

av varandra. En stor nackdel är att vätejonkoncentrationen, $\underline{h}$, är den enda fria halt, som är experimentellt mätbar. Detta förhållande försvårar tolkningen av mätdata. (Jfr nedan.) Trots denna inskränkning måste emellertid den potentiometriska metoden anses vara den mest fördelaktiga av de experimentella metoder som författaren har använt.

I oxalatsystemen bildas fasta faser redan vid låga värden på $\underline{C}_M$ och $\underline{C}_A$. Potentiometriska bestämningar är i dessa fall inte användbara. För Sc-oxalatsystemet har dock en del data kunnat erhållas från övermättade lösningar varvid endast ett begränsat $\underline{a}$ -område kunde undersökas.

Vid den potentiometriska bestämningen erhålles som primärdata sammanhörande värden på $\underline{C}_M$, $\underline{C}_H$, $\underline{C}_A$ och $\underline{h}$. Man kan här exempelvis beräkna följande storheter: (En $\underline{N}$ -basisk syra förutsättes).

$$\underline{a}^* = \frac{\underline{C}_H - \underline{h}}{\delta_1 \underline{h} + 2\delta_2 \underline{h}^2 + \dots + \underline{N} \cdot \delta_{\underline{N}} \cdot \underline{h}^{\underline{N}}}$$

$$\underline{n}^* = \frac{\underline{C}_A - \underline{a}^*(1 + \delta_1 \underline{h} + \delta_2 \underline{h}^2 + \dots + \delta_{\underline{N}} \underline{h}^{\underline{N}})}{\underline{C}_M}$$

Om endast komplex av typen $\text{MA}_{\underline{r}}^{\beta-2\underline{r}}$ bildas är $\underline{a}^* = \underline{a}$ och $\underline{n}^* = \underline{n}$. (Jfr ref. 11). Ur sammanhörande värden på $\underline{a}$ och $\underline{n}$ kan de olika $\beta_{\underline{j}}$ -värdena erhållas med ett antal standardmetoder.³⁹ Genom mätningar i lösningar med $\underline{C}_M = 0$ erhålles protoneringskonstanterna $\delta_{\underline{j}}$ på analogt sätt.

Den eventuella existensen av blandade komplex, $\text{M}_{\underline{p}}\text{H}_{\underline{q}}\text{A}_{\underline{r}}^{\beta+\underline{q}-2\underline{r}}$ i vilka $\underline{p} > 1$ och $\underline{q} \neq 0$, brukar oftast undersökas genom bestämning av funktionen $\underline{n}^*(\underline{a}^*)$ för lösningar där $\underline{C}_M$, $\underline{C}_H$ och $\underline{C}_A$ varieras

systematiskt. Endast då denna funktion är beroende av $\underline{C}_H$ och/eller $\underline{C}_M$ anses andra komplex än $MA_{\underline{r}}^{3-2\underline{r}}$ kunna förekomma i mätlösningarna. Det kan emellertid många gånger vara svårt att få en korrekt uppfattning om komplexbildningen på detta sätt. Ibland kan t ex ganska stora variationer av kvoten $\underline{C}_H/\underline{C}_A$ ge oförändrad $\bar{n}^*(\underline{a}^*)$ -funktion trots att relativt stora mängder sura komplex finns närvarande. En utförligare diskussion av dessa problem återfinnes i ref. 11.

Eu-IMDA-systemet (Potentiometri)

De preliminära titreringarna indikerade att blandade komplex bildades. Som nämnts tidigare är sura komplex sannolika i detta komplexsystem.

Eftersom andra metall-species än $EuA_{\underline{r}}^{3-2\underline{r}}$ -komplex med all säkerhet existerar kan den fria dikarboxylathalten, $\underline{a}$, ej beräknas på något enkelt sätt. En grafisk integrationsmetod, som beskrivits av Österberg⁴⁰, skulle i princip kunna användas för beräkning av $\underline{a}$. Man erhåller med denna metod värden på $\underline{a}/\underline{a}_0$, där $\underline{a}_0$ är en integrationskonstant. För att $\underline{a}_0$ skall kunna bestämmas måste mätningarna utsträckas till en så hög vätejonhalt att all komplexbildning är försumbar. Med stigande $\underline{h}$ -värde sjunker emellertid mätnoggrannheten i föreliggande fall. Trots den låga mätnoggrannheten gjordes likväl ett försök att bestämma $\underline{a}$ -värden för några preliminära mätningar. Det experimentella materialet vid relativt höga vätejonhalter kunde någorlunda väl beskrivas av komplexen EuA^+ och $EuHA^{2+}$. För de mindre sura lösningarna behandlades mätdata som om endast $EuA_{\underline{r}}^{3-2\underline{r}}$ -komplex existerade.

Dessa första ansatser gav approximativa värden på jämviktskonstanterna K_{101} , K_{102} , K_{103} och K_{111} .

För att kunna få en mer pålitlig beskrivning av mätdata användes (för det kompletta mätaterialet) en dator och ett minsta-kvadratprogram i serien "LETAGROP VRID", skrivet av N. Ingri och L.-G. Sillén⁴¹. Även protoneringskonstanterna (δ_1 - δ_3), som tidigare bestämts grafiskt, förfinades med denna metod. Dylika minsta-kvadratberäkningar har också utförts för de andra IMDA-systemen och för EDDA-systemen. Den "bästa" konstantuppsättningen vid denna LETAGROP-metod erhålles genom en minimering av felkvadratsumman, $\underline{U}$. Som felbärande variabel valdes $\underline{C}_H/\underline{C}_A$. Man får då:

$$\underline{U} = \sum_i [(C_{H,i,calc} - C_{H,i,exp})/\underline{C}_{A,i}]^2$$

$C_{H,i,calc}$ är det värde på den totala vätejonhalten, som beräknas från $\underline{C}_{A,i}$, $\underline{C}_{M,i}$, $\underline{h}_i$ och β_{pqr} -värdena.

Det aktuella LETAGROP-programmet har vissa begränsningar. Någon möjlighet till individuell viktning av de olika mätpunkterna föreligger inte. Vidare måste man själv avgöra vilka komplex, som skall medtagas vid beräkningarna. Man bör dessutom känna motsvarande jämviktskonstanter storleksordning någorlunda väl innan datorberäkningarna påbörjas. För det mesta ger dock denna minsta-kvadratmetod besked om vilken av två eller flera kombinationer av metallkomplex som bäst beskriver mätdata. Man måste emellertid efter en beräkning kontrollera om samtliga species finns närvarande i tillräckligt stora koncentrationer. För att man skall kunna påvisa ett komplex bör dess α_{pqr} -värde i allmänhet överstiga 0.05-0.10 inom ett inte alltför begränsat $\underline{a}$ -område.

De storheter som jämföres, då olika alternativ av metallkomplex provas, är t ex sig y, standarddeviationen för den felbärande variabeln, och $(\frac{C_{H,calc}}{C_A} - \frac{C_{H,exp}}{C_A})$ för de olika mätpunkterna. (Jämför ref. C.)

Mätdata kan med god noggrannhet beskrivas med hjälp av komplexen EuA^+ , EuA_2^- , EuA_3^{3-} , EuHA^{2+} och $\text{EuH}_2\text{A}^{3+}$. Sig y har ett lågt värde, 5.3×10^{-3} ; om endast fyra mätserier användes, (jfr ref. D, s. 4) sjunker sig y till 2.1×10^{-3} . $(\frac{C_{H,calc}}{C_A} - \frac{C_{H,exp}}{C_A})$ är praktiskt taget genomgående mycket liten (jfr tabell i ref. C, s. 1404). Resultat från minsta-kvadratberäkningarna återfinnes i ref. C, s. 1403 och tabell 2 i ref. D. Konstanterna $\underline{K}_1$ - $\underline{K}_3$, $\underline{K}_M$ och $\underline{K}_{M2}$ är angivna i tabell 3.

Om komplexen EuHA^{2+} och $\text{EuH}_2\text{A}^{3+}$ ej tas med vid beräkningarna får man en betydligt sämre beskrivning av mätdata. Om de suraste mätlösningarna uteslutes ger dock enbart komplexen EuA_r^{3-2r} ($r = 1-3$) en någorlunda god beskrivning av det experimentella materialet. De värden på β_{10r} som därvid erhålles skiljer sig emellertid från de slutgiltiga värdena med ungefär en faktor 2. (Jfr ref. C, s. 1406, r. 9-17.)

Några andra kombinationer av metallkomplex har också prövats för att undersöka om någon signifikant förbättring kunde erhållas vid beskrivningen av mätdata. En beräkning där EuHA_2 medtogs gav ett mycket osäkert värde på β_{112} och ett praktiskt taget oförändrat sig y-värde. Om detta komplex överhuvudtaget existerar är det närvarande i mycket små mängder. Liknande resultat erhöles när EuH_2A_2^+ och några flerkärniga komplex, t ex $\text{Eu}_2\text{A}_4^{2-}$ och $\text{Eu}_2\text{A}_5^{4-}$, testades.

Tabell 3. Stegrisa komplexbildningskonstanter ($\underline{K}_j$), jämviktskonstanter för reaktioner mellan M^{3+} och HA^- resp. H_2A ($\underline{K}_M$ och $\underline{K}_{M2}$) samt kvoter $\underline{K}_j/\underline{K}_{j+1}$. Konstantvärdena är mult. med M.

M^{3+}	A ²⁻	$\underline{K}_1 \times 10^{-5}$	$\underline{K}_2 \times 10^{-4}$	$\underline{K}_3 \times 10^{-3}$	$\underline{K}_4$	$\underline{K}_M$	$\underline{K}_{M2}$	$\underline{K}_1/\underline{K}_2$	$\underline{K}_2/\underline{K}_3$	$\underline{K}_3/\underline{K}_4$
Ce ³⁺	Oxalat	0.31	0.26	0.25	28	-	-	12	10	9
Eu ³⁺	"	1.10	0.45	0.74	34	-	-	24	6	22
Tb ³⁺	"	1.20	0.60	0.99	37	-	-	20	6	27
Lu ³⁺	"	1.90	1.79	1.62	87	-	-	11	11	19
Sc ³⁺	"	177	36	0.98	42	-	-	38	370	25
Pr ³⁺	IMDA	11.9	4.0	1.26	-	27	10	30	32	-
Er ³⁺	"	29	15.9	13.5	-	31	10	18	12	-
Ho ³⁺	"	14	21	21	-	23	9	21	11	-
Lu ³⁺	"	116	65	1.88	-	19	7	16	350	-
Sc ³⁺	"	7.0 · 10 ⁴	164	-	-	187	59	4.10 ³	-	-
La ³⁺	EDDA	90	4.0	-	-	50	18	240	-	-
Nd ³⁺	"	950	41	-	-	110	15	230	-	-
Sm ³⁺	"	1760	149	-	-	120	16	120	-	-
Tb ³⁺	"	1830	610	-	-	280	18	30	-	-
Er ³⁺	"	3200	2700	-	-	220	14	12	-	-
Yb ³⁺	"	6700	12900	-	-	240	11	5	-	-

Övriga IMDA-system (Potentiometri)

För de övriga tre lantanoid-IMDA-systemen har samma komplex antagits vara dominerande som i Eu-systemet. Även för dessa system fås en mycket god beskrivning av mätdata. (Sig y är 0.002-0.003.) Resultat från minsta-kvadratberäkningarna återfinnes i tabell 2 i ref. D. Konstanterna $\underline{K}_1$ - $\underline{K}_3$, $\underline{K}_M$ och $\underline{K}_{M2}$ är angivna i tabell 3.

Även det experimentella materialet från Sc-IMDA-systemet har tolkats med hjälp av komplexen $\underline{MA}_r^{3-2r}$, $\underline{MHA}^{2+}$ och $\underline{MH}_2A^{3+}$. Då data vid höga $\underline{a}$ -värden (dvs låga $\underline{h}$ -värden) är ganska osäkra kan existensen av $\underline{ScA}_3^{3-}$ ej avgöras. Det experimentella materialet tycks emellertid indikera att ett dylikt komplex är mycket svagt om det överhuvudtaget bildas. ($\underline{n}^*(\underline{a}^*)$ -kurvan uppvisar en tydlig platå vid $\underline{n}^* = 2$ för $10^{-5} M < \underline{a} < 10^{-4} M$.) Felet i β_{121} är stort och man kan ej med säkerhet uttala sig om förekomsten av $\underline{ScH}_2A^{3+}$. De övriga jämviktskonstanterna, β_{101} , β_{102} och β_{111} , har ej kunnat bestämmas med lika stor noggrannhet som motsvarande lantanoid-konstanter. Orsaken till detta kan vara att andra species, t ex hydroxokomplex, finns närvarande i förhållandevis större mängder än vad som är fallet i lantanoidsystemen. Jämviktskonstanterna återfinnes i ref. D och i tabell 3.

EDDA-systemen (Potentiometri)

Studierna av EDDA-systemen är i princip analoga med motsvarande IMDA-undersökningar. Den enda rimliga tolkningen av mätdata omfattar bl a sura komplex, vilka ej omnämnts tidigare

i litteraturen. I dessa system får man dock en god beskrivning av mätdata med endast MA^+ och MA_2^- om de suraste lösningarna ej medtages vid beräkningarna. De värden på β_{101} och β_{102} som härvid erhålles är för Sm ca 70 % av de slutliga konstantvärdena.

Följande komplex har använts vid tolkningen av mätdata: MA^+ , MA_2^- , MHA^{2+} och MH_2A^{3+} . Protonsystemet omfattar $H_gA^{g-2}-$ -species med $g = 1-4$. Existensen av MHA^{2+} kan dock ej avgöras enbart med ledning av experimentella data. α_{111} är nämligen alltid mycket liten och är t ex i Sm-systemet som mest ca 0.02. Att detta komplex likväl har tagits med beror på att det kan anses som tillräckligt "kemiskt sannolikt". (Jfr ref. C och ref. 11.) Värdena för β_{111} blir givetvis mycket osäkra men kan dock ge en viss antydning om styrkan av eventuellt förekommande MHA^{2+} -komplex. Det faktum att samtliga konstanter β_{111} är positiva och av samma storleksordning talar för att MHA^{2+} -species verkligen existerar. Resultat från minsta-kvadratberäkningarna återfinnes i tabell 3 i ref.E. Konstanterna K_1 , K_2 , K_3 och K_4 är givna i tabell 4.

Ce-oxalatsystemet

Detta system har undersökts med löslighetsmetodik. Experimentella detaljer återfinnes i ref. A, s. 97-101. Tre fasta faser, stabila i områden med olika oxalathalt, har använts. Den termodynamiskt stabila fasen vid de lägsta a -värdena är $Ce_2A_3 \cdot xH_2O$ medan den fas som är stabil vid de högsta oxalat-koncentrationerna har sammansättningen $Na_4Ce_2A_5 \cdot xH_2O$. I mellanområdet existerar $NaCeA_2 \cdot xH_2O$ som stabil fas. Efter publiceringen

av uppsats A har författaren upptäckt att saltet $\text{Na}_4\text{Ce}_2\text{A}_5$ tidigare finns beskrivet i litteraturen.⁴² (Jfr ref. A, s. 94, r. 4 nedifrån.)

Som primärdata erhålles lösligheten, $\underline{S}$, och sammansättningen i lösningen innan den fasta fasen har tillsatts. Ur dessa data beräknas halten $\underline{a}$ i de mättade lösningarna genom en iterationsmetod (jfr ref. A, s. 96). Om endast komplex av typen MA_j^{3-2j} bildas och den fasta fasen har sammansättningen $\text{Na}_{\underline{p}}\text{M}_{\underline{q}}\text{A}_{\underline{r}}$ erhålles följande samband: (Jfr ref. A, s. 95.):

$$\underline{S} = \underline{C}_M = \sum_{j=0}^J \text{MA}_j^{3-2j}$$

$$\underline{K} = [\text{Na}^+]^{\underline{p}} \cdot \underline{m}^{\underline{q}} \cdot \underline{a}^{\underline{r}}$$

Härur kan härledas

$$\underline{S} = \underline{K}^{1/\underline{q}} \sum_{j=0}^J \beta_j \cdot \underline{a}^{j-\underline{r}/\underline{q}} = \underline{K}^{1/\underline{q}} \cdot \underline{a}^{-\underline{r}/\underline{q}} \cdot \underline{X}$$

där $\underline{K} = \underline{K}[\text{Na}^+]^{-\underline{p}}$. $\underline{K}$ är en konstant eftersom Na^+ -halten hålles konstant = 1.00 M. Med hjälp av grafiska extrapolationsmetoder enligt Leden och Fronæus³⁹ kan de olika $\underline{K}^{1/\underline{q}} \cdot \beta_j$ -värdena beräknas. Konstanterna β_j erhålles tydligen om löslighetsprodukten, $\underline{K}$, är känd. Denna storhet kan dock endast bestämmas om $\underline{S}$ -data är tillgängliga vid låga A^{2-} -halter.

En del löslighetsdata har kunnat erhållas för samtliga faser i $\underline{a}$ -områden där den fasta fasen är metastabil. Detta beror på att den hastighet med vilken de olika fasta faserna omvandlas ibland är avsevärt lägre än den hastighet med vilken löslighetsjämvikten ställer in sig. För ett visst $\underline{a}$ -värde har

alltså olika $\underline{C}_M$ -värden kunnat erhållas (jfr fig. 1 i ref. A, s. 102). Härigenom har man kunnat konstatera att flerkärniga komplex ej bildas i någon betydelsefull mängd (jfr ref. A, s. 95 och ref. 43).

Löslighetsprodukten för Ce_2A_3 har kunnat bestämmas tämligen noggrant. De andra fasernas $\underline{K}$ -värden beräknades ur omvandlingspunkterna, dvs löslighetskurvornas skärningspunkter. (Se ref. A, s. 96-97.) Den slutliga konstantuppsättningen, som omfattar komplexen $\text{CeA}_{\underline{j}}^{3-2\underline{j}}$, $\underline{j} = 1-4$, beskriver hela mätmaterialet med god noggrannhet. De relativt stora avvikelser, som föreligger för fasen Ce_2A_3 i det metastabila området kan förklaras med att en fasomvandling har börjat ske. Konstanterna har uträknats med ett minsta-kvadratprogram, skrivet av C.-G. Ekström (jfr ref. A, s. 104). De stegvisa konstanterna ($\underline{K}_{\underline{j}}$) för Ce-oxalatsystemet och de andra i ref. A beskrivna oxalatsystemen, återfinnes i tabell 3. Eu, Tb-, Lu- samt proton-oxalatsystemet har studerats av I. Grenthe och E. Rundcrantz.

Sc-oxalatsystemet

Potentialmätningar har i Sc-oxalatsystemet endast kunnat utföras i ett relativt snävt $\underline{a}$ -område beroende på att fasta faser lätt bildas. Reproducerbarheten av mätningarna är dessutom ibland tämligen dålig. Orsaken är kanske att mätningarna utförts med övermättade lösningar. $\underline{n}^*(\underline{a}^*)$ -funktionen blir oförändrad inom felgränserna när kvoterna $\underline{C}_H/\underline{C}_A$ och $\underline{C}_A/\underline{C}_M$ varieras. Spridningen är emellertid så stor att man ej helt kan utesluta förekomsten av små mängder $\text{M}_{\underline{p}}\text{H}_{\underline{q}}\text{A}_{\underline{r}}^{3\underline{p}+\underline{q}-2\underline{r}}$ -species, t ex hydroxokomplex.

Mätdata har ej använts för att bestämma jämviktskonstanter.

$\bar{n}^*$ -värdena har endast jämförts med motsvarande data erhållna från löslighets- och extraktionsmätningarna.

I systemet bildas tre svårslösliga faser: $\text{Sc}_2\text{A}_3 \cdot x\text{H}_2\text{O}$, $\text{NaScA}_2 \cdot x\text{H}_2\text{O}$ och $\text{Na}_3\text{ScA}_3 \cdot x\text{H}_2\text{O}$. Löslighetsmätningar har utförts med användande av samtliga dessa faser. Tillförlitliga data kunde emellertid endast erhållas för Na_3ScA_3 . De storheter, som har kunnat beräknas, är $K \cdot \beta_j$; $j = 2-4$ där K är löslighetsprodukten för Na_3ScA_3 . Resultat återfinnes i tabell 5 i ref. B, s. 166. Av dessa värden är $K \cdot \beta_2$ ganska osäkert, eftersom ScA_2^- finns närvarande i jämförelsevis små mängder i det tillgängliga oxalathaltområdet.

Potential- och löslighetsmätningarna, som f ö täcker ungefär samma a -område (jfr figurer i ref. B), kan uppenbarligen inte ge någon tillförlitlig information om de två första komplexbildningsstegen, $\text{Sc}^{3+} + \text{A}^{2-} \rightarrow \text{ScA}^+$ och $\text{ScA}^+ + \text{A}^{2-} \rightarrow \text{ScA}_2^-$. För att erhålla en mer fullständig beskrivning av detta komplexsystem var det således nödvändigt att använda ytterligare en experimentell metod. En lämplig sådan är extraktionsmätningar. Dessa utfördes i a -intervallet $3 \cdot 10^{-8} \text{ M} - 6 \cdot 10^{-2} \text{ M}$. Experimentella detaljer ges i ref. B, s. 160. Man erhåller som primärdata fördelningskvoten för Sc mellan två vätskefaser. Sedan kan man lätt beräkna sammanhörande värden på X och a (jfr ref. B, s. 159). Även i detta fall användes ett minsta-kvadratprogram, skrivet av C.-G. Ekström, för bestämningen av β_j -värdena ($j = 1-4$). Resultaten återfinnes i tabell 5 i ref B, s. 166. I samma tabell anges också en slutlig konstantuppsättning för Sc-oxalatsystemet där värdena $\beta_1-\beta_3$ direkt har tagits från extraktionsundersökningen.

β_4 -värdet har erhållits ur sambandet $\beta_4 = K_4(\text{lösl.}) \cdot \beta_3(\text{extr.})$. De stegvisa konstanterna anges i tabell 3. β_i -värdena ger en god beskrivning av mätdata från samtliga metoder (jfr figurer i ref. B).

Slutkommentar angående existensen av $M_{p,q,r}$ -komplex

Beskrivningen av mätdata är - möjligen med undantag för Sc-IMDA-systemet - mycket god för de olika undersökta komplexsystemen. Enbart detta faktum är ett starkt indicium på att andra komplex än de antagna bör vara relativt betydelselösa. För att mer detaljerat kunnat styrka gjorda tolkningar av mätdata skall en del punkter närmare beröras.

a) Flerkärniga komplex. Variationen av C_M är relativt stor i samtliga komplexsystem. Speciellt stor variation fås i Sc-oxalatsystemet ($10^{-6} \text{ M} < C_M < 10^{-2} \text{ M}$). Den goda beskrivningen av mätdata visar att flerkärniga komplex är betydelselösa i samtliga komplexsystem. (Jfr också s. 15 och s. 19-20.)

b) Hydroxokomplex. Med hjälp av hydrolyskonstanterna³³⁻³⁶ och de framräknade jämviktskonstanterna kan man definitivt fastslå att $M(\text{OH})^{2+}$, $M_2(\text{OH})_2^{4+}$ och liknande species är försumbara. Sannolikheten för bildningen av "blandade" basiska komplex ($M_{p,q,r}$ -species med $q < 0$, $r > 0$) är svår att bedöma. Om konstanterna $K_B = \frac{h}{h} [M(\text{OH})A] \cdot [MA^+]^{-1}$ ej är större än hydrolyskonstanterna $\beta_{1-10} = \frac{h}{h} [M(\text{OH})^{2+}] \cdot [M^{3+}]^{-1}$ behöver man inte ta hänsyn till komplexen $M(\text{OH})A$. Värdena på β_{1-10} är för La, Y och Sc respektive 10^{-10} M , 10^{-9} M och 10^{-4} M . (Ref. 33-36.) Som jämförelse kan nämnas att K_B för lantanoid-EDTA-systemen är ca 10^{-12} M .

(Ref. 44.) Blandade basiska komplex har möjligen en viss betydelse i Sc-systemen (jfr s. 17 och s. 20).

c) Sura komplex. Om K_M -värdena för oxalatsystemen antages vara lika stora som β_1 -värdena för motsvarande acetatsystem (48 M^{-1} och 1400 M^{-1} för Ce resp Sc) blir α_{111} i de använda mätlösningarna som högst 0.14 (Ce) och 0.09 (Sc). Dessa första approximationer, baserade på antagandet att en liknande koordinationsstyp fås för väteoxalat och acetat, antyder att ett CeHA^{2+} -komplex eventuellt skulle kunna påvisas. Vissa resultat tyder dock på att motsvarande K_M -värde är lägre än ca 48 M^{-1} . I tabell 4 görs jämförelser mellan reaktionerna $\text{L} + \text{H}^+$ och $\text{L} + \text{M}^{3+}$, där L är olika ligander som koordineras på ungefär samma sätt. Det låga K_{S2} -värdet för oxalat indikerar att även K_M -värdet för Ce-oxalatsystemet är lågt, sannolikt mindre än ca 5 M^{-1} . I detta sammanhang kan också nämnas att man vid en undersökning av Eu(III)-oxalatsystemet med jonbytarmetodik³⁷ funnit belägg för existensen av komplexet EuHA^{2+} med K_M -värdet 30 M^{-1} . Eftersom Eu^{3+} -komplexen är starkare än motsvarande Ce^{3+} -komplex för exempelvis acetat^{1,3} och vätemalonat¹¹ bör K_M för Ce-oxalatsystemet enligt denna undersökning vara mindre än 30 M^{-1} . Under en sådan förutsättning kan CeHA^{2+} ej påvisas i de använda mätlösningarna.

Kalorimetriska mätningar

I de system där fasta faser ej bildas har förändringar i entalpi bestämts för de flesta av komplexbildningsreaktionerna. Mätningarna har utförts kalorimetriskt med användning av den

Tabell 4. Jämförelser mellan protonupptagningen $\text{Ligand} + \text{H}^+$ och komplexbildningsreaktionen $\text{Ligand} + \text{M}^{3+}$. Motsvarande jämnviktskonstanter betecknas $\underline{K}_\alpha$ och $\underline{K}_\beta$. (För samtliga ligander utom acetat är $\underline{K}_\alpha = \underline{K}_{\text{S2}}$, $\underline{K}_\beta = \underline{K}_{\text{M}}$. För acetat är $\underline{K}_\alpha = \underline{K}_{\text{S}}$ och $\underline{K}_\beta = \beta_1$.) $\underline{K}_\alpha$ och $\underline{K}_\beta$ i tabellen repr. konstantvärdena mult. med M.

Ligand	M^{3+}	$\underline{K}_\alpha$	$\underline{K}_\beta$	$\underline{K}_\alpha / \underline{K}_\beta$	$\log \underline{K}_\alpha$	$\log \underline{K}_\beta$	$\log \underline{K}_\alpha / \log \underline{K}_\beta$	Ref.
Väteoxalat, HOOC-COO^-	Ce^{3+}	10.2	-	-	1.01	-	-	A
Vätemalonat, $\text{HOOC-CH}_2\text{-COO}^-$	Pr^{3+}	388	26	15	2.59	1.41	1.8	11
Vätesuccinat, $\text{HOOC-(CH}_2)_2\text{-COO}^-$	Pr^{3+}	$1.58 \cdot 10^4$	52	300	4.20	1.72	2.4	59
Vätetiodiacetat, $\text{HOOC-CH}_2\text{-S-CH}_2\text{-COO}^-$	Pr^{3+}	$1.36 \cdot 10^3$	29	47	3.13	1.46	2.1	17
Väte-IMDA, $^-\text{OOC-CH}_2\text{-NH}_2^+\text{-CH}_2\text{-COO}^-$	Pr^{3+}	376	27	14	2.58	1.43	1.3	D
Glycin, $\text{NH}_3^+\text{-CH}_2\text{-COO}^-$	Ce^{3+}	575	3.4	170	2.76	0.53	5.2	60
Acetat, $\text{CH}_3\text{-COO}^-$	Pr^{3+}	$4.1 \cdot 10^4$	65	630	4.61	1.81	2.5	1

kalorimeter, som beskrivits av Grenthe, Ots och Ginstrup.¹² Primärvärden är det avgivna värmets (Q) vid varje tillsats av titrerlösning samt totalhalterna (C_H , C_M och C_A). De olika Q -värdena korrigeras sedan för utspädningsvärmen, varvid storheterna Q_{corr} erhålles. Eftersom totalhalterna och jämviktskonstanterna är kända kan koncentrationerna av de olika komplexen beräknas i varje titrerpunkt. Ur sammanhörande värden på Q_{corr} och dessa sistnämnda koncentrationer kan entalpiförändringarna erhållas. I föreliggande fall har $\Delta H_{\text{pqr}}^{\circ}$ -värdena beräknats med hjälp av ett program i LETAGROP-serien (LETAGROP KALLE⁴⁵).

Vid de slutliga minsta-kvadratförfiningarna har neutralisationsreaktionen $H^+ + OH^- \rightarrow H_2O$ medtagits (jfr s. 6 i ref. D). Entalpivärdena förändras dock föga om beräkningarna göres utan hänsyn till denna reaktion. Hydrolysjämvikter i vilka $M(OH)^{2+}$ och $M_2(OH)_2^{4+}$ ingår har helt kunnat försummas (jfr s. 6 i ref. D).

För lantanoid-IMDA-systemen erhålles ΔH_{10r}° -värden med ganska små fel medan ΔH_{111}° -värdena är något mer osäkra. ΔH_{121}° -data har relativt stora fel, sannolikt beroende på att β_{121}° -värdena är förhållandevis osäkra. Felen i konstanterna är troligen större än vad LETAGROP-beräkningarna antyder. Anledningen till detta är att α_{121} alltid är förhållandevis liten. För Eu-systemet är detta värde som mest 0.10 (potentiometri) respektive 0.12 (kalorimetri).

Beträffande EDDA-systemen har endast ΔH_{011}° , ΔH_{021}° , ΔH_{101}° och ΔH_{102}° beräknats. Två av dessa system (Gd och Tb) har författaren ej tidigare undersökt potentiometriskt. Motsvarande jämviktskonstanter uppskattades med hjälp av Thompsons resultat,⁴⁶ erhållna vid jonstyrkan 0.1 M, och egna jämviktsvärden

för andra lantanoider. De olika $\Delta H^{\circ}_{\text{pqr}}$ -värdena beskriver mätdata förhållandevis bra.

Entropidata har beräknats ur sammanhörande värden på ΔH° och ΔG° ur sambandet $\Delta S^{\circ} = (\Delta H^{\circ} - \Delta G^{\circ})/T$.

Resultat av minsta-kvadratförfiningarna från IMDA- och EDDA-systemen återfinnes i tabell 5 i ref. D och tabell 6 i ref. E. Värdena ΔH° och ΔS° med index j, M och M2 är angivna i tabell 5 och 6.

Jämförelser med tidigare undersökningar

Åtskilliga bestämningar av proton-IMDA-systemet har utförts (jfr ref. C). De värden på δ_1 och δ_2 som har erhållits vid författarens mätningar överensstämmer bra med de flesta av de tidigare bestämda konstanterna. Existensen av H_3A^+ har man oftast ej tagit hänsyn till i de äldre arbetena. Undantag är exempelvis en studie av Al^{3+} -IMDA-systemet.⁴⁷ Vid de tidigare studierna av metall-IMDA-systemen (ref. C) har man vidare ej beaktat förekomsten av MHA^{2+} , MH_2A^{3+} och (med något undantag) MA_3^{3-} . Detta faktum kan eventuellt förklara skillnaderna i erhållna β_{101} - och β_{102} -värden. Några entalpibestämningar för IMDA-systemen är ej gjorda förut bortsett från en undersökning⁴⁸ där ΔH° för reaktionerna $H^+ + A^{2-} \rightarrow HA^-$, $La^{3+} + A^{2-} \rightarrow LaA^+$ och $LaA^+ + A^{2-} \rightarrow LaA_2^-$ bestämdes. De resultat som därvid erhöles var: -34.1 kJ/mol, 0.7 kJ/mol och -1.4 kJ/mol. De två sista värdena överensstämmer dåligt med författarens resultat; jfr tabell 5.

Få studier har gjorts av EDDA-system. (Se tabell 7.) De i ref. E angivna konstanterna δ_1 och δ_2 skiljer sig något från

Tabell 5. Termodynamiska storheter för IMDA-systemen.

Storheterna är dividerade med kJ/mol.

Metall- jon	$-\Delta G_1^{\circ}$	$-\Delta G_2^{\circ}$	$-\Delta G_3^{\circ}$	$-\Delta G_M^{\circ}$	$-\Delta G_{M2}^{\circ}$
Pr ³⁺	34.7	26.2	17.7	8.1	5.6
Eu ³⁺	36.9	29.7	23.6	8.6	5.8
Ho ³⁺	37.9	30.4	24.6	7.8	5.4
Lu ³⁺	40.5	33.2	18.7	7.3	4.7

Metall- jon	$-\Delta H_1^{\circ}$	$-\Delta H_2^{\circ}$	$-\Delta H_3^{\circ}$	$-\Delta H_M^{\circ}$	$-\Delta H_{M2}^{\circ}$
Pr ³⁺	3.6	7.4	9.9	-4.2	7.0
Eu ³⁺	3.7	12.8	16.6	-4.8	5.0
Ho ³⁺	-1.5	7.6	28.1	-7.0	7.3
Lu ³⁺	0.6	8.4	23.4	-7.6	10.4

Metall- jon	$T\Delta S_1^{\circ}$	$T\Delta S_2^{\circ}$	$T\Delta S_3^{\circ}$	$T\Delta S_M^{\circ}$	$T\Delta S_{M2}^{\circ}$
Pr ³⁺	31.1	18.8	7.8	12.3	-1.4
Eu ³⁺	33.2	16.9	7.0	13.4	0.8
Ho ³⁺	39.4	22.6	-3.5	14.6	-1.9
Lu ³⁺	39.7	24.8	-4.7	14.9	-5.7

Tabell 6. Termodynamiska storheter för EDDA-systemen.

Storheterna är dividerade med kJ/mol.

Metall- jon	$-\Delta G_1^{\circ}$	$-\Delta H_1^{\circ}$	$T\Delta S_1^{\circ}$	$-\Delta G_2^{\circ}$	$-\Delta H_2^{\circ}$	$T\Delta S_2^{\circ}$
La ³⁺	39.7	4.7	35.0	26.2	8.5	17.7
Nd ³⁺	45.5	10.1	35.0	32.0	8.7	23.3
Sm ³⁺	47.1	12.2	34.9	35.2	13.0	22.2
Gd ³⁺	46.7	8.9	37.8	36.0	16.1	19.9
Tb ³⁺	47.2	4.8	42.4	38.7	17.4	21.3
Dy ³⁺	47.8	6.5	44.3	40.3	16.3	24.0
Er ³⁺	48.6	1.4	47.2	42.4	13.2	29.4
Yb ³⁺	50.4	5.2	47.2	46.3	15.9	30.4

Tabell 7. Översikt av olika författares EDDA-studier. I = jonstyrka.

I/M och neutralsalt	Temp.	$\log(\delta_1 \cdot M)$	$\log(\delta_2 \cdot M^2) -$ $-\log(\delta_1 \cdot M)$	Ref.
0.1	30 °C	9.46	6.42	49
0.1 KNO ₃	25 °C	9.57	6.46	46
0.1 KNO ₃	"	9.58	6.52	50
0.1 KNO ₃	"	9.84	6.67	51
1 NaClO ₄	"	9.69	6.72	E

I/M och neutralsalt	Temp.	M ³⁺	$\log(K_1 \cdot M)$	$\log(K_2 \cdot M)$	Ref.
0.1 KNO ₃	25 °C	La ³⁺	7.04	4.73	46
1 NaClO ₄	"	"	6.26	4.60	E
0.1 KNO ₃	"	Nd ³⁺	8.06	5.63	46
"	"	"	8.30	5.60	51
1 NaClO ₄	"	"	7.98	5.61	E
0.1 KNO ₃	"	Sm ³⁺	8.28	6.07	46
1 NaClO ₄	"	"	8.25	6.17	E
0.1 KNO ₃	"	Tb ³⁺	8.18	6.52	46
1 NaClO ₄	"	"	8.26	6.79	E
0.1 KNO ₃	"	Er ³⁺	8.59	7.45	46
1 NaClO ₄	"	"	8.51	7.43	E
0.1 KNO ₃	"	Yb ³⁺	8.93	7.92	46
1 NaClO ₄	"	"	8.83	8.11	E

äldre undersökningar.^{46,49-51} En förklaring kan kanske vara att de tidigare författarna ej tagit hänsyn till H_3A^+ och H_4A^{2+} . De två konstanterna β_{101} och β_{102} har bestämts av andra forskare.^{46,51} Resultaten från samtliga dessa arbeten stämmer tämligen väl överens.

De flesta tidigare undersökningar, som gjorts av M^{3+} -oxalatsystem^{24,25,37} är ofullständiga och sannolikt mer eller mindre tvivelaktiga. Orsaken till detta är t ex för snävt a-område (ref. B, s. 158) och bristfällig experimentell teknik (ref. A, s. 94 och s. 106-107). Den nogrannaste av de tidigare undersökningarna torde vara en studie av Sekine. (Se tabell 8.) Hans resultat överensstämmer väl med de i ref. A angivna konstanterna (jfr tabell 3). Sekine har emellertid inte arbetat vid tillräckligt höga A^{2-} -halter för att kunna påvisa några MA_4^{5-} -komplex.

Tabell 8. Jämviktskonstanter för oxalatsystem, bestämda av

T. Sekine. (1 M NaClO₄, 25 °C.) Ref.: Sekine, T. Acta Chem. Scand. 19 (1965) 1476. I tabellen återfinnes också ett par konstantuppsättningar från ref. A.

Metalljon	$\log(\underline{K}_1 \cdot M)$	$\log(\underline{K}_2 \cdot M)$	$\log(\underline{K}_3 \cdot M)$	Ref.
La ³⁺	4.26	3.59	2.42	Sekine
Eu ³⁺	4.77	3.95	2.67	"
"	5.04	3.65	2.87	A
Lu ³⁺	5.11	4.07	3.61	Sekine
"	5.28	4.25	3.21	A
Am ³⁺	4.63	3.72	2.80	Sekine

AVSLUTANDE DISKUSSION

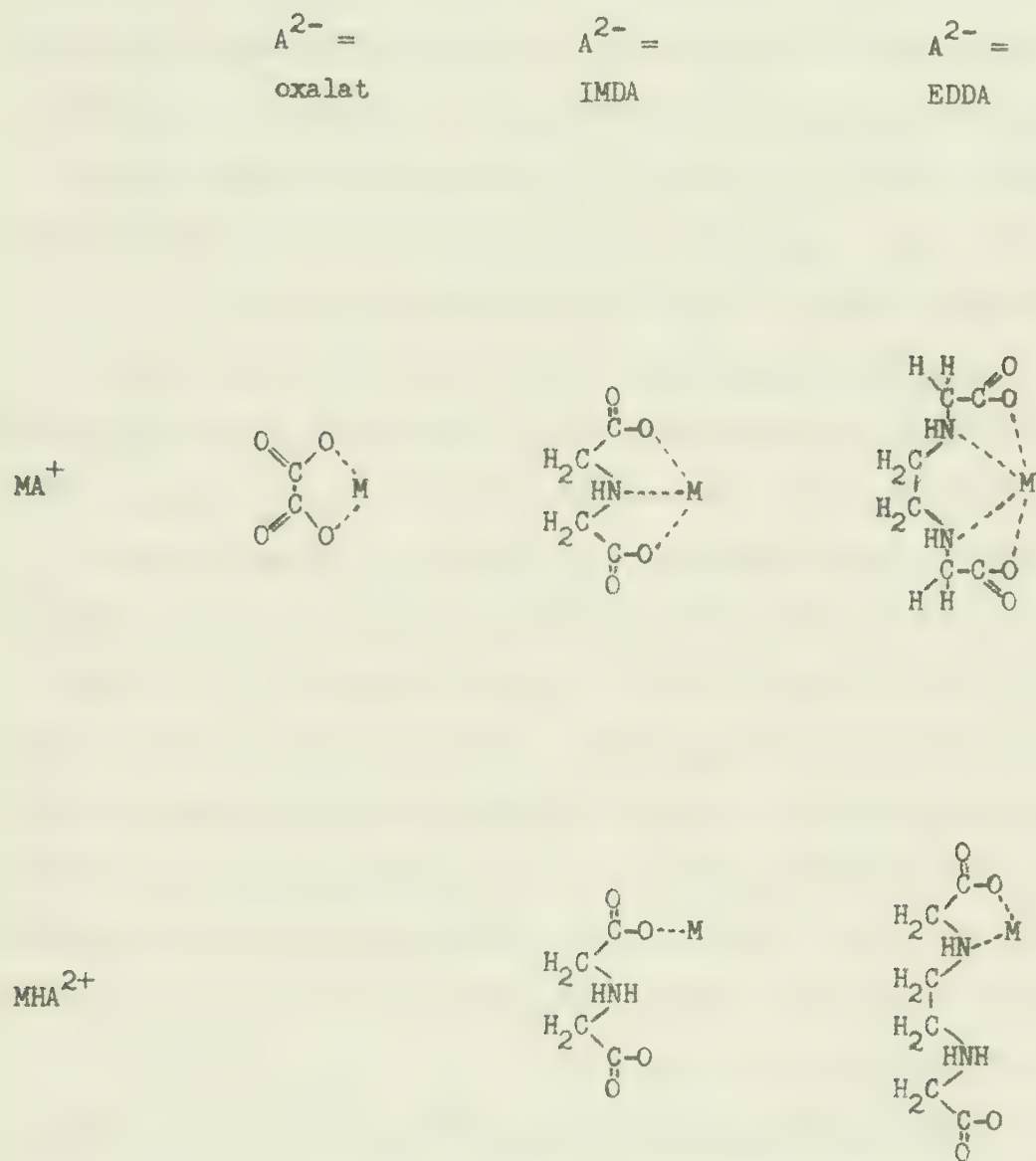
De i inledningen nämnda problemställningarna skall här behandlas. (Jfr s. 4.)

Koordinationssättet för de olika metallkomplexen

MA_{j-2j} -komplex. De olika β_j -värdena för oxalat, IMDA och EDDA är så pass stora att kelatkomplex med all säkerhet bildas mellan M^{3+} och de olika A^{2-} -jonerna (jfr tabell 3). De mest sannolika koordinationssätten visas i fig. 3. Av tidigare undersökta ligander bör malonat¹¹ och maleinat¹⁶ koordinera på liknande sätt som oxalat, dvs ett syre från varje karboxylatgrupp är donatoratom. Med IMDA helt analoga komplex fås med stor sannolikhet för dipikolinat,² diglykolat⁴ och tiodiacetat.¹⁷ Iminokvävet hos IMDA är i dessa ligander ersatt med pyridinkväve, etersyre och etersvavel. Dessa antaganden rörande koordinationstypen styrks av strukturundersökningar av analoga komplex i fast fas.²¹

MHA^{2+} (IMDA-systemen). De låga K_M -värdena (tabell 3), vilka är av samma storleksordning som β_1 -värdena i acetatsystemen,^{1,3} antyder att kelat ej bildas hos MHA^{2+} -komplexen. Stöd för denna hypotes fås vidare genom en strukturundersökning av föreningen $Nd_2A_3 \cdot 2HCl \cdot 7H_2O$.²² Sannolikt ger HA^- och acetatjonen en likartad koordination. (Jfr fig. 3). Vätemalonat¹¹ och vätetiodiacetat¹⁷ koordinerar med all säkerhet på samma sätt. K_M -värdena för motsvarande Pr-system är $26 M^{-1}$ resp. $29 M^{-1}$.

Figur 3. Sannolika koordinationsätt för komplexen MA^+ och MHA^{2+}



MH_2A^{3+} (IMDA-systemen). K_{M2} -värdena är mindre än motsvarande K_M -värden. (Se tabell 3.) Kvoterna K_M/K_{M2} är ungefär lika med de statistiskt förväntade faktorerna för liganderna väteiminodiacetat, HA^- , och iminodiättiksyra, H_2A . (Två fria karboxylatgrupper i första fallet, bara en i det andra.) Detta tyder på att också H_2A koordinerar på samma sätt som acetatjonen. Något annat realistiskt alternativ kan dessutom knappast föreligga; jfr strukturformeln i fig. 2.

MHA^{2+} (EDDA-systemen). Jonen HA^- har tre potentiella donatoratomer: två karboxylsyren och ett iminokväve. K_M -värdena är mycket osäkra; jfr tabell 3 i ref. E. ($K_M = \beta_{111}/\beta_{011}$.) Motsvarande EDG-konstanter kan bestämmas med betydligt större precision.¹⁸ För Gd-EDG-systemet har följande värden erhållits: $\beta_{011} = (5.23 \pm 0.04) \cdot 10^3 \text{ M}^{-1}$, $\beta_{111} = (1.22 \pm 0.14) \cdot 10^6 \text{ M}^{-2}$, $K_M = 233 \text{ M}^{-1}$. Det faktum att K_M -värdena är ungefär lika stora för EDDA och EDG talar för att de förstnämnda jämviktskonstanterna är av rätt storleksordning. Det mest troliga koordinationssättet visas i fig. 3. Kelatbildning får anses vara relativt sannolik eftersom "acetatkoordination" borde ha resulterat i mindre jämviktskonstanter; jfr tabell 3.

MH_2A^{3+} (EDDA-systemen). K_M -värdena för EDDA-systemen är ungefär lika stora som K_M - och K_{M2} -värdena för IMDA-systemen; jfr tabell 3. En "acetatlik" koordination är således sannolik även i detta fall. Andra koordinationssätt torde dessutom vara uteslutna på grund av ligandens utseende; jfr fig. 2.

Donatoregenskaper hos olika atomer

IMDA, diglykolat och tiodiacetat är geometriskt analoga.

(Jfr fig. 1.) β_1 för motsvarande Pr-komplex är $1.2 \cdot 10^6 \text{ M}^{-1}$, $2 \cdot 10^5 \text{ M}^{-1}$ och $7 \cdot 10^2 \text{ M}^{-1}$. Dessa resultat överensstämmer med tidigare undersökningar,^{24,25} vilka utvisar att svavel har sämre donatoregenskaper än kväve och syre vid koordination med lantanoidjoner. (Jfr s. 1.) I detta fall kan den låga jämviktskonstanten för tiodiacetat delvis bero på svårigheter att packa liganden runt centraljonen.

Jämförelser mellan EDDA och EDG är också av intresse i detta sammanhang. För Gd-systemen erhålles följande resultat (EDDA resp. EDG): $\underline{K}_1 = 1.6 \cdot 10^8$ och $1.0 \cdot 10^5 \text{ M}^{-1}$; $\underline{K}_2 = 2 \cdot 10^6$ och $1.0 \cdot 10^3 \text{ M}^{-1}$. Tydligt ger iminokvävena här betydligt starkare komplex än etersyrena. (Jfr IMDA kontra diglykolat ovan.) Skillnaderna mellan dessa två ligander kan bättre belysas då entalpi- och entropidata har erhållits för EDG-systemen.

Både $-\Delta H_j^0$ - och ΔS_j^0 -värdena är genomgående högre för dipikolinat⁵ än för IMDA; jfr tabell 9. Detta gäller samtliga tre komplexbildningssteg. Den stora elektronrörligheten i pyridinringen ger uppenbarligen bättre donatoregenskaper hos pyridinkvävet än hos iminokvävet. Vidare kan man anta att donatoratomerna i dipikolinat är praktiskt taget fixerade i lämpliga koordinationslägen medan IMDA uppvisar större böjlighet och rotationsförmåga.

Effekten av olika atomantal i kelatringen

De tvåtandade liganderna oxalat,¹¹ malonat¹¹ och maleinat¹⁶ ger med all säkerhet komplex med respektive 5, 6 och 7 atomer i kelatringen. Konstanten β_1 för motsvarande Ce-system är $3 \cdot 10^4 \text{ M}$

Tabell 9. Jämförelser mellan termodynamiska storheter från dipi-
kolinat- och IMDA-system. $\Delta(-\Delta H_j^{\circ}) = -\Delta H_{j,dip.}^{\circ} - (-\Delta H_{j,IMDA}^{\circ})$;
 $\Delta(T\Delta S_j^{\circ}) = T\Delta S_{j,dip.}^{\circ} - T\Delta S_{j,IMDA}^{\circ}$. Storheterna är dividerade med
kJ/mol. (Referenser: 5 och D.)

M^{3+}	$\Delta(-\Delta H_1^{\circ})$	$\Delta(-\Delta H_2^{\circ})$	$\Delta(-\Delta H_3^{\circ})$
Pr ³⁺	12.7	9.1	4.7
Eu ³⁺	13.3	8.3	2.6
Ho ³⁺	9.6	10.0	2.8
Lu ³⁺	8.6	7.5	4.5

M^{3+}	$\Delta(T\Delta S_1^{\circ})$	$\Delta(T\Delta S_2^{\circ})$	$\Delta(T\Delta S_3^{\circ})$
Pr ³⁺	1.6	1.2	5.0
Eu ³⁺	0.1	2.5	5.0
Ho ³⁺	2.1	1.2	6.4
Lu ³⁺	2.4	3.4	3.1

$2 \cdot 10^3 \text{ M}^{-1}$ och $6 \cdot 10^2 \text{ M}^{-1}$. Starkast komplexbildning fås tydligen när en femring uppstår. Detta antal atomer ger nästan alltid störst stabilitet vid ringslutningar för likartade ligander. Man brukar förklara detta förhållande på följande sätt: Ju mindre antal atomer, som ingår i ringen, desto mer sannolik blir kelatbildningen. Detta medför att ΔS -termen för komplexbildningsreaktionen ökar. Å andra sidan uppträder vid minskat atomantal allt starkare spänningar för denna ringslutningsprocess, vilket orsakar att ΔH -termen blir större. En femring innebär oftast en kompromiss med samtidig hög bildningssannolikhet och låg spänning.

Variationen av termodynamiska storheter genom lantanoidserien.

Variationen av olika liganders ΔH_j^0 - och ΔS_j^0 -värden genom lantanoidserien är av speciellt intresse, jfr inledningsavsnittet. IMDA och EDDA ger ett mönster likartat med det som erhålles för dipikolinat och diglykolat.^{5,7} I fig. 1-4 i ref. E visas termodynamiska data som funktion av atomnumret för de tre första liganderna; jfr också tabell 5, 6 och 9. Även andra komplexbildare, exempelvis tiodiacetat¹⁷ och nitrilotriacetat,⁵² $\text{N}(\text{CH}_2\text{COO}^-)_3$, uppvisar en likartad variation. Förklaringen till detta gemensamma beteende är eventuellt en förändring i hydratationstillståndet någonstans i lantanoidserien både för de enkla metalljonerna och de komplexa jonerna.⁵³⁻⁵⁷ Beträffande metalljonerna tyder vissa undersökningar på att en ändring av hydratationstalet sker omkring Gd^{3+} . (Ref 53.) Dylika variationer i hydratationstal är också möjliga för de komplexa jonerna. En alternativ förklaring till de termodynamiska storheternas variation är att koordinationsgeometrin förändras i de olika MA_{j-2j-1} -komplexen ($j \geq 0$).⁵³

För liganderna IMDA, malonat¹⁶ och tiodiacetat¹⁷ kan man lämpligen jämföra de olika termodynamiska storheterna för reaktionerna $M^{3+} + HA^- \rightarrow MHA^{2+}$ med motsvarande storheter för reaktionen $M^{3+} + Ac^- \rightarrow MAc^{2+}$ (Ac^- = acetat).⁶ Variationen genom lantanoidserien förefaller att vara någorlunda likartad för samtliga dessa ligander. Detta faktum tycks bl a bekräfta de tidigare gjorda antagandena beträffande koordinationssätt.

Entalpi- och entropidata för reaktionerna $M^{3+} + H_2A \rightarrow MH_2A^{3+}$ (A^{2-} = IMDA) har så stora fel att några meningsfulla jämförelser ej kan göras.

Maximalt koordinationstal och steriska hinder.

Oxalatsystemen. I oxalatsystemen komplexbindes maximalt fyra ligander, vilket sannolikt ger ett koordinationstal av åtta i det mättade komplexet (MA_4^{5-}). Undersökningar av de fasta faserna $M_2A_3 \cdot nH_2O$ ²¹ visar att 9-koordination föreligger för de flesta lantanoiderna (La-Tm). Koordinationstalet 8 uppträder i slutet av lantanserien (Yb, Lu) samt för Sc. Både 8- och 9-koordination erhålles för fasen $M_2A_3 \cdot nH_2O$ i ett övergångsområde (Ho, Er, Tm). För dessa 9-koordinerade oxalat i fast fas är varje metalljon omgiven av tre A^{2-} -joner och tre H_2O -molekyler.

I lantanoidsystemen bildas de högsta komplexen (MA_3^{3-} och MA_4^{5-}) utan några svårigheter. Detta kan utläsas från värdena på kvoterna $\frac{K_i}{K_{i+1}}$. (Se tabell 3.) För Sc-oxalatsystemet bildas motsvarande species ej lika lätt. (Se tabell 3 och jämför ref. B, s. 167.) Anledningen till detta är sannolikt något "steriskt hinder". På grund av skillnaden i jonstorlek kommer

de koordinerade donatoratomerna närmare varandra i Sc^{3+} -komplexen än i motsvarande lantanoidkomplex. Detta förhållande är väl belagt i fast fas där jonradieminskningen t ex orsakar en krympning av enhetscellen.²¹ Ibland fås också en annan struktur eller ett ändrat koordinationsstal för de tyngsta lantanoiderna och Sc.²¹ (Jfr ovan.)

IMDA-systemen. Det maximala koordinationsstalet för lantanoidsystemen är säkerligen 9 i vattenlösning, eftersom högst tre ligander koordinerar. Utseendet för $\bar{n}(\underline{a})$ -kurvorna vid de högsta värdena ($2.9 < \bar{n} < 3.0$) visar tydligt att ett fjärde komplex är mycket osannolikt. I fast fas är koordinationsstalet för lantanoidföreningarna $[\text{MA}(\text{H}_2\text{O})_3]\text{Cl}$ ($\text{M} = \text{Pr-Lu}$)²¹ också 9. Till metalljonen koordineras här en kelatbildande ligand (A^{2-}), tre karboxylsyren från angränsande ligander och tre H_2O -molekyler. För $\text{M}_2\text{A}_3 \cdot 2\text{HCl} \cdot 7\text{H}_2\text{O}$ ($\text{M} = \text{Ce-Gd}$) fås 8-koordination: Sex karboxyl- och två vattensyren omger metalljonen. Inget kelat bildas här utan varje ligand koordinerar med sina fyra karboxylsyren till fyra olika metalljoner.

Kvoten $\underline{K}_2/\underline{K}_3$ är förhållandevis hög i Lu-systemet; jfr tabell 3. Detsamma gäller för diglykolat- och dipikolinatsystemen i slutet av lantanoidserien.^{2,4} (ΔS_3^0 -värdena är mycket låga i samtliga dessa fall. Jfr ref. 5 och tabell 5.) Redan det andra Sc-IMDA-komplexet bildas med stor svårighet; se tabell 3. Något värde på β_3 för detta system föreligger inte. Mätningarna tycks dock utvisa att ett tredje komplex är mycket svagt om det överhuvudtaget bildas. Förhållandet är likartat i Sc-diglykolat- och Sc-dipikolinatsystemen.¹⁰

EDDA-systemen. I dessa system bör koordinationsstalet 8

erhållas i lösning eftersom jonen A^{2-} här är fyrtandad och högst två ligander koordineras. $\bar{n}(a)$ -kurvorna visar att ett komplex MA_3^{3-} troligen helt kan uteslutas. Några steriska hinder föreligger uppenbarligen inte när komplexet MA_2^- bildas. Kvoterna K_1/K_2 är t o m högst för de lägsta atomnumren; jfr tabell 3 och ΔH_2^0 -värdena i fig. 4 i ref. E. Någon fullständig strukturundersökning har hittills ej utförts för analoga EDDA-föreningar i fast fas. Några ryska forskare⁵⁸ har för saltet $NdANO_3 \cdot 1.33 H_2O$ bestämt gitterparametrar samt gjort IR-mätningar. Med ledning av de sistnämnda undersökningarna drar de slutsatsen att kväve koordineras till metalljonen samt att både en- och tvåtandade karboxylatgrupper förekommer.

REFERENSER

1. Sonesson, A. On the Complex Chemistry of the Tervalent Rare-Earth Ions, (Diss.), Lund 1961.
2. Grenthe, I. J. Am. Chem. Soc. 83 (1961) 360.
3. Grenthe, I. Acta Chem. Scand. 16 (1962) 1695.
4. Grenthe, I. och Tobiasson, I. Acta Chem. Scand. 17 (1963) 2101.
5. Grenthe, I. Acta Chem. Scand. 17 (1963) 2487.
6. Grenthe, I. Acta Chem. Scand. 18 (1964) 285.
7. Grenthe, I. Acta Chem. Scand. 18 (1964) 293.
8. Grenthe, I. och Williams, D.R. Acta Chem. Scand. 21 (1967) 341.
9. Grenthe, I. och Williams, D.R. Acta Chem. Scand. 21 (1967) 347.
10. Grenthe, I. och Hansson, E. Acta Chem. Scand. 23 (1969) 611.
11. Dellien, I. och Grenthe, I. Acta Chem. Scand. 25 (1971) 1387.
12. Grenthe, I., Ots, H. och Ginstруп, O. Acta Chem. Scand. 24 (1970) 1067.
13. Grenthe, I. och Ots, H. Acta Chem. Scand. (Under tryckning.)
14. Grenthe, I. och Ots, H. Acta Chem. Scand. (Under tryckning.)
15. Dellien, I. och Grenthe, I. Skall publiceras.
16. Dellien, I. och Malmsten, L.-Å. Skall publiceras.
17. Dellien, I., Grenthe, I. och Hessler, G. Skall publiceras.
18. Grenthe, I. Skall publiceras.

19. Ryhl, T. Studies on Dissociation Rates on some Lanthanoid EDTA Complexes (Diss.), Lund 1971.
20. Uppsatser som skall publiceras. (C.-G. Ekström, T. Ryhl m fl.)
21. Uppsatser (14 st) i serien "Structural Studies on the Rare Earth Carboxylates", vilka har eller kommer att publiceras i Acta Chem. Scand. (Första publ. år 1968.) Författare: Albertsson, J., Grenthe, I., Hansson, E. och Oskarsson, Å.
22. Albertsson, J. och Oskarsson, Å. Acta Chem. Scand. 22 (1968) 1700.
23. Ahrland, S., Chatt, J. och Davies, N.R. Quart. Rev. 12 (1958) 265.
24. Martell, A.E. och Sillén, L.-G. Stability Constants of Metal-Ion Complexes, Spec. Publ. No 17, The Chem. Soc., London 1964.
25. Martell, A.E. och Sillén, L.-G. Stability Constants of Metal-Ion Complexes, Supplement No 1, Spec. Publ. No 25, The Chem. Soc., London 1971.
26. Moeller, T., Martin, D.F., Thompson, L.C., Ferrús, R., Feistel, G.R. och Randall, W.J. Chem. Rev. 65 (1965) 1.
27. Eyring, L. Progress in the Science and Technology of the Rare Earths, Volume 3 (Chap. 3). Pergamon Press, Glasgow, 1968.
28. Beineke, T.A. och Delgaudio, J. Inorg. Chem. 7 (1968) 715.
29. Martin, D.S., Rundle, R.E. och Golden, S.A. J. Chem. Phys. 24 (1956) 1114.
30. Melson, G.A. och Stoltz, R.W. Coord. Chem. Rev. 7 (1971) 133.
31. Milligan, W.O. och Vernon, L.W. J. Phys. Chem. 56 (1952) 145.
32. Mooney, R.C.L. Acta Cryst. 2 (1956) 677.

33. Biedermann, G. och Ciavatta, L. Acta Chem. Scand. 15 (1961) 1347.
34. Biedermann, G. och Ciavatta, L. Arkiv Kemi 22 (1964) 253.
35. Biedermann, G., Kilpatrick, M., Pokras, L. och Sillén, L.-G. Acta Chem. Scand. 10 (1956) 1327.
36. Aveston, J. J. Chem. Soc. (A) 1966 1599.
37. Paramonova, V.I., Kereichuk, A.S. och Chizhov, Radiokhimiya 5 (1963) 63.
38. Coetzee, C.J. och Freiser, H. Anal. Chem. 40 (1968) 2071.
39. Rossotti, F.J.C. och Rossotti, H. The Determination of Stability Constants, Mc Graw, New York, Toronto, London 1961.
40. Österberg, R. Acta Chem. Scand. 14 (1960) 471.
41. Ingri, N. och Sillén, L.-G. Arkiv Kemi 23 (1965) 97.
42. Štěrbá-Böhme, J. och Písaříček, A. Coll. Czech. Chem. Comm. 2 (1936) 244.
43. Johansson, L. Coord. Chem. Rev. 3 (1968) 293.
44. Merbach, A. och Gnägi, F. Chimia 23 (1969) 271.
45. Arnek, R. Arkiv Kemi 32 (1970) 81.
46. Thompson, L.C. J. Inorg. Nucl. Chem. 24 (1962) 1083.
47. Liberti, A. och Napoli, A. J. Inorg. Nucl. Chem. 33 (1971) 89.
48. Anderegg, G. Helv. Chim. Acta 47 (1964) 1801.
49. Chaberek, S. Jr och Martell, A.E. J. Am. Chem. Soc. 74 (1952) 6228.

50. da Silva, J.J.R.F. och Simões, M.L.S. J. Inorg. Nucl. Chem. 32 (1970) 1313.
51. Sevost'yanova, N.I., Martynenko, L.I. och Spitsyn, V.I. Russ. J. Inorg. Chem. 15 (5) (1970) 633.
52. de la Praudiere, P.L.E. och Staveley, L.A.K. J. Inorg. Nucl. Chem. 26 (1964) 1713.
53. Spedding, F.H. och Atkinson, G. i Hamer, J.W. The Structure of Electrolytic Solutions, Wiley, New York 1959 (Kap. 22).
54. Hoard, J.L., Byunkook, Lee och Lind, M.D. J. Amer. Chem. Soc. 87 (1965) 1612.
55. Geier, G., Karlén, U. och v. Zelewsky, A. Helv. Chim. Acta 52 (1969) 1967.
56. Geier, G. och Karlén, U. Helv. Chim. Acta 54 (1971) 135.
57. Anderegg, G. och Wenk, F. Helv. Chim. Acta 54 (1971) 216.
58. Sevost'yanova, N.I., Belyaeva, K.F. och Martynenko, L.I. Zh. Strukt. Khim. 12 (1) (1971) 182.
59. Ke, C.M., Kong, P.C., Cheng, M.S. och Li, N.C. J. Inorg. Nucl. Chem. 30 (1968) 961.
60. Tanner, S.P. och Choppin, G.R. Inorg. Chem. 7 (1968) 2046.

Ref. A

Thermodynamic Properties of Rare Earth Complexes

VI. Stability Constants for the Oxalate Complexes of Ce(III), Eu(III), Tb(III), and Lu(III)

INGMAR GRENTHE, GÖRAN GARDHAMMAR and
ESKIL RUNCRAANTZ

Division of Physical Chemistry, Chemical Center, University of Lund, Box 740, S-220 07 Lund 7, Sweden

The solubilities of different sparingly soluble oxalates of trivalent cerium, europium, terbium, and lutetium have been determined at various oxalate concentrations. The solid phases were $M_2A_3 \cdot xH_2O$, $NaMA_2 \cdot xH_2O$, and $Na_4M_3A_5 \cdot xH_2O$ where A denotes the oxalate ion and M one of the lanthanoids. Solubility products and stability constants for four mono-nuclear oxalate complexes of each lanthanoid were determined from the solubility data. The constants refer to a temperature of 20.0° and a medium containing 1 M $Na^+(ClO_4^-)$ as neutral salt.

The lanthanoid complexes for which the most solution chemistry information is available contain polydentate carboxylates as ligands. The experiments have shown that all rare earth elements form complexes of the same type with a given ligand. If the ratios of the stepwise stability constants are considered, individual differences are noticed. *E.g.* for the tridentate ligands oxydiacetate¹ and 2,6-pyridino-dicarboxylate² one can notice that the ratio between the second and third stepwise stability constant is increasing rapidly from erbium to lutetium. In other words, there is an increased difficulty for the third complex to be formed for the last elements in the lanthanoid series. This "steric effect" is probably caused by a combination of a decrease in the ionic radius of the central ion and the special geometric requirements of the ligand.

The present work is part of a systematic investigation of lanthanoid dicarboxylate complexes from which we hope to get a better understanding of the various factors of importance for complex formation in solution. We have chosen oxalate as a ligand because it is the simplest of the dicarboxylate ions and we want to determine:

a. The composition and the concentrations of the various oxalate complexes formed in solution.

X-Ray structure determinations of various rare-earth compounds have shown that the coordination number of these elements is always larger than six in the solid state.³ Several investigations strongly suggest that this is also the case in solution. In this connection it is of special interest to investigate if a fourth oxalate complex is formed in solution.

b. The possible occurrence of individual variations of the stepwise stability constants which can be interpreted as due to "steric effects" of the type discussed before.

Lanthanoide oxalate complexes have been studied by experimental methods such as solubility,⁴⁻⁶ ion-exchange,⁷ and solvent-extraction.⁸ All investigators agree that strong oxalate complexes are formed but the opinions differ about the maximum number of coordinated oxalate groups.

The most reliable of these investigations is a solvent-extraction study by Sekine,⁸ whose results will be compared with our own in the discussion.

The results of the solubility measurements published so far are questionable in two ways:

a. The authors have not used a medium with constant ionic strength. Therefore the activity coefficients of all the species participating in the equilibria have to be determined. The practical impossibility of this task has been pointed out several times, *e.g.* by Rossotti and Rossotti.⁹

b. When interpreting the solubility data the possibility of the formation of a solid solution or a phase transition must always be kept in mind. Phase transitions occur (*vide infra* p. 101) in the rare earth oxalate systems, a fact which escaped the earlier investigators.

In this study we have investigated the complex formation in solution by means of the solubility method, and using in most cases more than one solid phase. For two elements, europium and terbium, we have also made a solvent-extraction study of solutions with high oxalate concentrations and in this way extended the measurements of Sekine.⁸ All measurements have been performed in a medium with constant sodium-ion concentration, *viz.* 1.00 M, and a temperature of 20.0°C.

SOLUBILITY MEASUREMENTS

The lanthanoide elements form several sparingly soluble oxalates. All of these can be described by the general formula $N_p M_q A_r \cdot x H_2O$, where N is one of H, Na, K, or NH_4 , M is a trivalent lanthanoide and A is oxalate. The best known compounds have the composition $M_2 A_3 \cdot x H_2O$, where the most common value of x is 10. Solid phases with this general composition are in the following referred to as phase I. Solids with the general formula $NaMA_2 \cdot x H_2O$ are referred to as phase II. In the course of this investigation we have discovered a third oxalate phase (phase III) of the composition $Na_4 Ce_2 A_5 \cdot 11 H_2O$.

In contact with an aqueous solution, the various phases are thermodynamically stable in different ranges of oxalate concentrations. Phase I is stable

at the lowest oxalate concentrations and is in equilibrium with phase II at a first transition point where the oxalate concentration equals $[A]_t$. In the case of cerium a second transition point, where phase II is in equilibrium with phase III, occurs at a still higher oxalate concentration, $[A]_r$. All solid phases have constant composition as far as we have been able to judge.

In many cases the phase-transitions are so slow that the solubility of a phase can be determined even in solutions where the phase is metastable (cf. p. 101).

Calculation of stability constants from solubility data

In the solutions, complexes of the general composition M_iA_j are formed between the rare-earth elements and the oxalate ion. The stability constants are denoted $\beta_{i,j}$ where:

$$\beta_{i,j} = \frac{[M_iA_j]}{[M]^i[A]^j} \quad (i \geq 1; j \geq 0; \beta_{1,0} \equiv 1) \quad (1)$$

If $[M]$ and $[A]$ refer to the concentration of lanthanoide ion and oxalate ion in a saturated solution, the solubility, S , and the solubility product, K , may be written:

$$S = \sum_{i=1}^I \sum_{j=0}^J i \beta_{i,j} [M]^i [A]^j \quad (2)$$

$$K = [Na]^p [M]^q [A]^r \quad (3)$$

Hence

$$S = \sum_{i=1}^I \sum_{j=0}^J i \beta_{i,j} K^{i/q} [Na]^{-pi/q} [A]^{j-(ri/q)} \quad (4)$$

If the sodium ion concentration is kept constant throughout the series of measurements we obtain

$$S = \sum_{i=1}^I \sum_{j=0}^J i \beta_{i,j} K^{i/q} [A]^{j-(ri/q)} \quad (5)$$

where:

$$K = K[Na]^p$$

It is obvious from eqn. (5) that several sets of i, j can give the same value of the exponent $[j-(ri/q)]$. Hence it is not possible to distinguish between mono- and polynuclear complexes from solubility measurements using only *one* solid phase. This dilemma disappears if solubility data are available from at least two solid phases with different values of r/q . Eqn. (5) takes the following forms for the three phases

$$S_I [A]^{3/2} \cdot K_I^{-1} = 1 + (\beta_{1,1} + 3\beta_{3,4} \cdot K_I + \dots) [A] + (\beta_{1,2} + \dots) [A]^2 + \dots + (2\beta_{2,1} K_I^2 + 4\beta_{4,4} K_I^4 + \dots) [A]^{-1} + \dots \quad (5, I)$$

$$S_{\text{II}}[A]^2 \cdot K_{\text{II}}^{-1} = (1 + 3\beta_{3,4}K_{\text{II}}^2 + \dots) + (\beta_{1,1} + 3\beta_{3,5}K_{\text{II}}^2 + \dots)[A] + (\beta_{1,2} + \dots)[A]^2 + \dots \quad (5, \text{II})$$

$$S_{\text{III}}[A]^{5/2} \cdot K_{\text{III}}^{-1} = 1 + (\beta_{1,1} + 3\beta_{3,6}K_{\text{III}}^2 + \dots)[A] + (\beta_{1,2} + \dots)[A]^2 + \dots + (2\beta_{2,1}K_{\text{III}}^2 + \dots)[A]^{-3/2} + \dots \quad (5, \text{III})$$

The coefficients for $[A]^i$ can be determined from these expressions, *e.g.* by the extrapolation methods of Leden and Fronæus^{9, p. 102} or by some least-squares method (Letagrop) using a high-speed digital computer. If the various coefficients turn out to have the same value for different solid phases it has been proved that the system is mononuclear.

In order to calculate the concentration of free oxalate ions in the saturated solutions the following method was adopted: The total concentration of ligand, C_A , in equilibrium with the solid phase is equal to

$$C_A = C_A' + (r/q)S \quad (6)$$

where C_A' is the total ligand concentration before any solid phase has been added. The oxalate ion is a fairly strong base with protonation constants δ_1 and δ_2 . Taking the protonated species into account we can write eqn. (6) for the mononuclear case as

$$C_A = [A](1 + \delta_1 h + \delta_2 h^2) + \sum_{i=1}^J j[\text{MA}_i] \quad (7)$$

The free oxalate concentration can now be calculated from the relation

$$[A] = \{C_A' - (\bar{n} - \frac{r}{q})S\}(1 + \delta_1 h + \delta_2 h^2)^{-1} \quad (8)$$

obtained from eqns. (6), (7) and the definition of the average ligand number, $\bar{n}$.

$\bar{n}$ is obtained from the solubility curve ($\log S$ vs. $\log[A]$) using the expression

$$\frac{d \log S}{d \log[A]} = \bar{n} - \frac{r}{q} \quad (9)$$

An iterative procedure has to be used in the calculation of the free oxalate concentration. As a first approximation the term $(\bar{n} - r/q)S$ may be neglected in comparison with C_A' . A preliminary solubility curve is plotted from which values of $\bar{n}$ can be obtained using eqn. (9). Using this set of $\bar{n}$ -values a new and more accurate value of $[A]$ is calculated. Further iteration did not improve this value.

It is necessary to have solubility data at low oxalate concentrations in order to determine that various solubility products. This is not always possible for phase II and III as they are thermodynamically unstable at small oxalate concentrations. The solubility products must then be calculated from the experimental values of the oxalate concentration at the phase transition point and the solubility product of the phase I (resp. II).

The transition $\text{I} \longrightarrow \text{II}$ may be described by



At the point of transition where the two solid phases both are in equilibrium with the solution we have

$$S_I = S_{II} \text{ and } K_I^{\frac{1}{2}}[A]_t^{-3/2} = K_{II}[A]_t^{-2}$$

$$\text{i.e. } K_{II} = (K_I[A]_t)^{\frac{1}{2}} \quad (10)$$

In the same way we obtain for the phase transition $II \longrightarrow III$:



$$\text{and } K_{III} = K_{II}^2[A]_T \quad (11)$$

Experimental

Chemicals used. Stock solutions of the various lanthanoid perchlorates and sodium perchlorate were prepared and analysed as described before.^{10,11} Stock solutions of oxalic acid and sodium oxalate (Merck *p.a.*) were analysed by cerimetric titrations. All radio-active tracers (¹⁴⁴Ce, ¹⁵²⁺¹⁵⁴Eu, ¹⁶⁰Tb, and ¹⁷⁷Lu) were obtained from the Radiochemical Centre, Amersham, U.K.

The rare earth oxalates were prepared in the following way: $\text{M}_2\text{A}_3 \cdot x\text{H}_2\text{O}$ were obtained by precipitating the rare-earth perchlorate solutions with oxalic acid. $\text{NaMA}_3 \cdot x\text{H}_2\text{O}$ was prepared by shaking phase I with a 75 mM sodium oxalate solution, with the sodium concentration equal to 1 M, or by precipitating the rare-earth solution with an excess of sodium oxalate. In the cerium case the oxalate concentration must be kept smaller than 14 mM because $\text{Na}_4\text{Ce}_2\text{A}_5 \cdot 11\text{H}_2\text{O}$ is formed if higher oxalate concentrations are used. This phase was prepared by shaking phase II with a solution containing a sodium oxalate concentration of 75 mM and a sodium perchlorate concentration of 1.00 M. Radioactive oxalates were prepared in the same way from lanthanoid stock-solutions of known specific activity.

Analyses of solid phases. The Eu, Tb, and Lu contents of the various oxalates was determined by burning the solids in a platinum crucible, dissolving the oxide in hydrochloric acid and titrating with EDTA after evaporation of the excess acid. The cerium contents of the various cerium oxalates was determined by direct oxidation of the oxalates with peroxodisulphate followed by a titration with Fe(II). The oxalate content was

Table 1. Analyses of the various rare earth oxalate phases.

Solid phase	% lanthanoid		% oxalate		% sodium		% carbon		% hydrogen	
	exptl.	calc.	exptl.	calc.	exptl.	calc.	exptl.	calc.	exptl.	calc.
$\text{Ce}_2\text{A}_3 \cdot 10\text{H}_2\text{O}$	38.7	38.7	36.3	36.4	—	—	10.2	10.0	3.3	2.8
$\text{NaCeA}_2 \cdot 6\text{H}_2\text{O}$	31.1	31.3	39.0	39.4	5.01	5.14	10.9	10.7	3.0	2.7
$\text{Na}_4\text{Ce}_2\text{A}_5 \cdot 11\text{H}_2\text{O}$	27.6	27.7	43.3	43.6	9.5	9.1	12.4	11.9	2.3	2.2
$\text{Eu}_2\text{A}_3 \cdot 10\text{H}_2\text{O}$	35.0	35.3	40.6	40.6	—	—	9.8	9.6	2.8	2.7
$\text{NaEuA}_2 \cdot 3.5\text{H}_2\text{O}$	42.6	42.5	36.9	36.7	5.52	5.55	—	—	—	—
$\text{Tb}_2\text{A}_3 \cdot 10\text{H}_2\text{O}$	34.6	34.6	41.9	41.7	—	—	9.6	9.5	2.9	2.7
$\text{NaTbA}_2 \cdot 3\text{H}_2\text{O}$	43.0	42.7	36.9	38.6	5.61	5.58	11.9	11.7	1.7	1.5
$\text{Lu}_2\text{A}_3 \cdot 7\text{H}_2\text{O}$	47.3	47.3	35.6	35.7	—	—	10.0	9.7	1.8	1.9
$\text{NaLuA}_2 \cdot 4\text{H}_2\text{O}$	38.9	39.2	39.4	39.5	—	5.15	10.9	10.8	2.3	1.8

Table 2. Experimental data for the determination of the protonation constants of the oxalate ion. The results are given as $C_{\text{H}_2\text{A}}$ (mM); $E - E_{\text{d}}$ (mV); $(h - h_{\text{calc}}) \times 10^4$ (M). The total oxalate concentration is constant, and equal to 50.00 mM. E is the measured emf and E_{d} the diffusion potential.^{1, p. 2107}

$C_{\text{H}_2\text{A}}$, $E - E_{\text{d}}$, $h - h_{\text{calc}}$: 5.00, 125.6, -0.004 ; 10.00, 100.8, 0.005 ; 20.00, 59.0, 0.14 ; 25.40, 28.9, -0.5 ; 26.95, 19.9, -0.2 ; 28.05, 14.3, -0.3 ; 28.90, 10.7, -1.1 ; 29.60, 7.3, 0.4 ; 30.00, 6.1, -1.2 ; 30.55, 4.4, -2.3 ; 36.30, -11.9 , -3.2 ; 40.00, -19.4 , 0.00 ; 45.00, -27.0 , -0.3 ; 50.00, -32.9 , 0.00 .

Table 3. Experimental data for the determination of the protonation constants for the oxalate ion at different total concentrations. The results are given as C_{A} (mM), $E - E_{\text{d}}$ (mV), $(h - h_{\text{calc}}) \times 10^4$ (M).

Series 1. $C_{\text{H}_2\text{A}}/C_{\text{Na}_2\text{A}} = 9:1$. C_{A} , $E - E_{\text{d}}$, $(h - h_{\text{calc}}) \times 10^4$: 5.00, 22.8, -0.6 ; 10.00, 6.9, -0.1 ; 20.00, -8.5 , 0.8 ; 50.00, -27.0 , -0.3 ; 100.0, -39.3 , -3.0 .
Series 2. $C_{\text{H}_2\text{A}}/C_{\text{Na}_2\text{A}} = 1:9$. C_{A} , $E - E_{\text{d}}$, $(h - h_{\text{calc}}) \times 10^4$: 5.00, 126.9, 0.9 ; 10.00, 126.6, -1.0 ; 20.00, 126.5, -2.5 ; 50.00, 125.6, -0.4 ; 100.0, 125.6, -1.0 .

determined by cerimetric titrations. Carbon and hydrogen were determined by elemental analyses, and sodium was analysed using a flame photometer. All phases were also characterised by their X-ray powder patterns. An X-ray structure investigation of the various solid oxalates is in progress.¹² The results of the analyses are collected in Table 1.

Solubility measurements. The solubility was investigated using two different methods. In the first method a small amount of active lanthanoide oxalate was equilibrated with 20 ml oxalate solution in a 100 ml glass flask. Equilibrium was attained by slow agitation in a thermostatted bath. The two phases were separated by filtration through a filter stick and the solubility was determined by measuring the activity of a 5.00 ml sample of the oxalate solution in a γ -scintillation detector (Landis & Gyr, EQP 3.1). Equilibrium was attained after 10–30 min but an equilibration time of 24 h was nevertheless used in most cases.

In the second method we used a solubility column of the Brønsted type.¹³ This is a more handy method to work with and has been used for obtaining most of our solubility data. The height of the oxalate column was approximately 1 cm and equilibrium was established after one passage of the oxalate solution through the column. The composition of the various oxalate solutions used in the solubility experiments are given in Tables 5 and 6. The sodium ion concentration is constant at 1.00 M in all solutions.

Table 4. Experimental determinations of the various phase transition points. The "best" values are given in the last column. The errors are estimated maximum errors.

Metal	Type of phase transition	Graphical determination	Two-phase determination	Determination from solubility prod.	"Best" value of transition points
		[A] (M)	[A] (M)	[A] (M)	[A] (M)
Ce	I $\rightarrow$ II	$(2.5 \pm 0.1) \times 10^{-4}$	$(1.0 \pm 0.1) \times 10^{-4}$		$(2.5 \pm 0.1) \times 10^{-4}$
	II $\rightarrow$ III	$(1.4 \pm 0.1) \times 10^{-2}$	$(1.6 \pm 0.2) \times 10^{-2}$		$(1.5 \pm 0.1) \times 10^{-2}$
Eu	I $\rightarrow$ II	$(7.6 \pm 1.2) \times 10^{-6}$	$(5.9 \pm 0.5) \times 10^{-6}$	$(8 \pm 2) \times 10^{-6}$	$(6.7 \pm 0.7) \times 10^{-6}$
Tb	I $\rightarrow$ II	$(1.45 \pm 0.1) \times 10^{-6}$	$(1.29 \pm 0.06) \times 10^{-6}$	$(1.45 \pm 0.25) \times 10^{-6}$	$(1.45 \pm 0.10) \times 10^{-6}$

Table 5. Experimental values of $\log S$ and $\log[A]$ for the cerium and lutetium oxalate systems. $\log S_{\text{calc}}$ is calculated with the final solubility products and stability constants of Table 8.

Lu(III), phase II $C_A^0 = 1.000 \text{ mM}$						Ce(III), phase I $C_A^0 = 10.00 \text{ mM}$					
$-\log h$	$-\log [A]$	$-\log S$	$\log \frac{S}{S_{\text{calc}}}$	$\bar{n}$		$-\log h$	$-\log [A]$	$-\log S$	$\log \frac{S}{S_{\text{calc}}}$	$\bar{n}$	
0.921	5.820	3.608	-0.024	0.24		1.377	4.330	5.128	0.011	0.69	
0.921	5.819	3.605	-0.020	0.24		1.377	4.330	5.140	-0.001	0.69	
Lu(III), phase II $C_A^0 = 10.00 \text{ mM}$						Ce(III), phase I $C_A^0 = 10.00 \text{ mM}$					
0.495	5.674	3.820	0.016	0.31		1.495	4.180	5.240	0.011	0.81	
0.495	5.674	3.811	0.025	0.31		1.495	4.180	5.249	0.002	0.81	
0.602	5.493	4.120	0.012	0.42		1.620	4.029	5.361	-0.016	0.94	
0.602	5.493	4.119	0.013	0.42		1.620	4.029	5.356	-0.011	0.94	
0.721	5.295	4.431	0.002	0.56		1.770	3.855	5.424	0.005	1.10	
0.721	5.295	4.425	0.008	0.56		1.770	3.855	5.424	0.005	1.10	
0.824	5.129	4.668	-0.006	0.68		1.886	3.726	5.509	-0.036	1.22	
0.824	5.129	4.671	-0.009	0.68		1.886	3.726	5.492	-0.019	1.22	
0.921	4.976	4.852	-0.001	0.82		1.886	3.726	5.475	-0.002	1.22	
0.921	4.976	4.853	-0.002	0.82		2.026	3.576	5.519	-0.014	1.36	
1.000	4.856	4.994	-0.007	0.93		2.026	3.576	5.519	-0.008	1.36	
1.000	4.856	4.990	-0.003	0.93		2.026	3.576	5.505	-0.000	1.36	
1.097	4.713	5.127	0.003	1.06		2.097	3.501	5.520	-0.007	1.43	
1.097	4.713	5.129	0.001	1.06		2.097	3.501	5.509	0.004	1.43	
1.180	4.594	5.239	-0.004	1.17		2.222	3.373	5.553	-0.039	1.55	
1.180	4.594	5.246	-0.011	1.17		2.222	3.373	5.517	-0.003	1.55	
1.268	4.474	5.334	-0.006	1.28		2.398	3.198	5.509	-0.018	1.72	
1.268	4.474	5.324	0.004	1.28		2.398	3.198	5.509	-0.018	1.72	
1.377	4.330	5.412	0.010	1.42		2.523	3.078	5.487	-0.032	1.84	
1.377	4.330	5.412	0.010	1.42		2.523	3.078	5.472	-0.017	1.84	
1.495	4.181	5.485	0.012	1.57		2.921	2.725	5.293	-0.015	2.18	
1.495	4.181	5.489	0.008	1.57		2.921	2.725	5.306	-0.028	2.18	
1.770	3.856	5.595	-0.007	1.88		2.921	2.725	5.301	-0.023	2.18	
1.770	3.856	5.595	-0.007	1.88		3.222	2.497	5.197	-0.099	2.41	
1.886	3.726	5.599	-0.003	2.00		3.222	2.497	5.127	-0.029	2.41	
1.886	3.726	5.601	-0.006	2.00		3.222	2.497	5.210	-0.112	2.41	
2.026	3.575	5.596	-0.010	2.14		3.523	2.315	5.024	-0.106	2.59	
2.026	3.575	5.597	-0.011	2.14		3.523	2.315	5.029	-0.111	2.59	
2.097	3.501	5.582	-0.009	2.21		Ce(III), phase II $C_A^0 = 10.00 \text{ mM}$					
2.097	3.501	5.582	-0.009	2.21		2.026	3.576	5.524	-0.001	1.36	
2.222	3.373	5.537	0.002	2.32		2.026	3.576	5.530	-0.007	1.36	
2.222	3.373	5.540	-0.001	2.32		2.097	3.501	5.580	-0.013	1.43	
2.398	3.198	5.451	0.018	2.48		2.097	3.501	5.583	-0.016	1.43	
2.398	3.198	5.451	0.018	2.48		2.222	3.373	5.658	-0.025	1.55	
2.523	3.078	5.374	0.030	2.59		2.222	3.373	5.640	-0.007	1.55	
2.523	3.078	5.325	0.003	2.80		2.398	3.198	5.702	-0.005	1.72	
2.523	3.078	5.321	0.007	2.80		2.398	3.198	5.713	-0.016	1.72	
2.953	2.699	5.129	-0.007	2.90		2.523	3.078	5.727	-0.004	1.84	
2.953	2.699	5.151	-0.029	2.90		2.523	3.078	5.730	-0.007	1.84	
3.184	2.524	4.965	-0.012	3.03		2.745	2.875	5.723	0.003	2.03	
3.184	2.524	4.965	-0.012	3.03		2.745	2.875	5.738	-0.002	2.03	
3.523	2.316	4.757	-0.035	3.19		2.921	2.725	5.718	0.003	2.18	
3.551	2.302	4.683	0.022	3.20		2.921	2.725	5.711	0.000	2.18	
4.398	2.060	4.355	0.039	3.38		3.222	2.497	5.650	0.004	2.41	
						3.222	2.497	5.646	0.008	2.41	
Lu(III), phase II C_A^0 varying $-\log h = 6.000$						Ce(III), phase I $C_A^0 = 1.000 \text{ mM}$					
$C_A^0 \cdot 10^3 \text{ (M)}$	$-\log [A]$	$-\log S$	$\log \frac{S}{S_{\text{calc}}}$	$\bar{n}$		$-\log h$	$-\log [A]$	$-\log S$	$\log \frac{S}{S_{\text{calc}}}$	$\bar{n}$	
14.00	1.859	4.072	0.031	3.52		0.521	5.773	3.385	-0.013	0.65	
28.00	1.561	3.600	0.022	3.70		0.921	5.781	3.607	-0.046	0.65	
28.00	1.561	3.611	0.011	3.70		Ce(III), phase II C_A^0 varying $-\log h = 6.000$					
37.50	1.436	3.406	0.000	3.76		$C_A^0 \cdot 10^3 \text{ (M)}$	$-\log [A]$	$-\log S$	$\log \frac{S}{S_{\text{calc}}}$	$\bar{n}$	
37.50	1.436	3.401	0.005	3.76		14.00	1.856	5.180	0.006	3.05	
50.00	1.312	3.203	-0.017	3.81		20.00	1.858	5.181	0.005	3.05	
50.00	1.312	3.199	-0.012	3.81		24.00	1.701	5.008	0.004	3.20	
Ce(III), phase I $C_A^0 = 1.000 \text{ mM}$						28.00	1.701	5.007	0.005	3.20	
$-\log h$	$-\log [A]$	$-\log S$	$\log \frac{S}{S_{\text{calc}}}$	$\bar{n}$		28.00	1.555	4.988	0.004	3.33	
0.921	5.773	3.385	-0.013	0.65		28.00	1.555	4.989	0.010	3.33	
0.921	5.781	3.607	-0.046	0.65		37.50	1.428	4.680	-0.003	3.43	
Ce(III), phase I $C_A^0 = 10.00 \text{ mM}$						37.50	1.428	4.684	0.004	3.43	
$-\log h$	$-\log [A]$	$-\log S$	$\log \frac{S}{S_{\text{calc}}}$	$\bar{n}$		50.00	1.303	4.475	-0.008	3.53	
0.495	5.655	3.490	0.038	0.06		50.00	1.303	4.476	-0.009	3.53	
0.495	5.667	3.530	-0.013	0.06		Ce(III), phase II $C_A^0 = 10.00 \text{ mM}$					
0.602	5.489	3.782	-0.004	0.09		$-\log h$	$-\log [A]$	$-\log S$	$\log \frac{S}{S_{\text{calc}}}$	$\bar{n}$	
0.602	5.489	3.770	0.010	0.09		14.00	1.856	5.180	-0.003	3.05	
0.721	5.292	4.031	0.020	0.14		20.00	1.701	5.074	0.006	3.20	
0.721	5.292	4.045	0.006	0.14		24.00	1.701	5.008	0.005	3.20	
0.824	5.127	4.279	-0.008	0.19		28.00	1.555	4.989	0.000	3.33	
0.824	5.127	4.273	-0.002	0.19		28.00	1.555	4.989	0.010	3.33	
0.921	4.975	4.454	0.011	0.26		37.50	1.428	4.680	-0.003	3.43	
0.921	4.975	4.457	0.008	0.26		37.50	1.428	4.684	0.004	3.43	
1.000	4.855	4.622	-0.012	0.32		50.00	1.303	4.475	-0.008	3.53	
1.000	4.855	4.611	-0.009	0.32		50.00	1.303	4.476	-0.009	3.53	
1.097	4.712	4.758	0.015	0.40		Ce(III), phase III $C_A^0 = 10.00 \text{ mM}$					
1.097	4.712	4.760	0.013	0.40		$-\log h$	$-\log [A]$	$-\log S$	$\log \frac{S}{S_{\text{calc}}}$	$\bar{n}$	
1.180	4.594	4.891	0.007	0.48		14.00	1.856	5.180	-0.003	3.05	
1.180	4.594	4.905	-0.007	0.48		20.00	1.701	5.074	0.006	3.20	
1.268	4.474	5.013	0.001	0.57		24.00	1.701	5.008	0.005	3.20	
1.268	4.474	5.002	0.012	0.57		28.00	1.555	4.989	0.000	3.33	

Table 6. Experimental values of $\log S$ and $\log[A]$ for the europium and terbium oxalate systems. $\log S_{\text{calc}}$ is calculated with the final solubility products and stability constants of Table 8.

Tb(III), phase I $C_A = 1.000$ (mM)						Eu(III), phase I $C_A = 1.000$ (mM)					
$-\log h$	$-\log [A]$	$-\log S$	$\log \frac{S}{S_{\text{calc}}}$	$\bar{n}$		$-\log h$	$-\log [A]$	$-\log S$	$\log \frac{S}{S_{\text{calc}}}$	$\bar{n}$	
0.321	6.504	2.840	0.002	0.04		0.32	6.631	3.045	-0.036	0.02	
0.321	6.504	2.840	0.002	0.04		0.321	6.637	3.054	-0.034	0.02	
0.487	6.347	3.065	0.006	0.05		0.487	6.452	3.219	-0.067	0.04	
0.487	6.338	3.051	-0.031	0.05		0.447	5.441	3.282	-0.013	0.34	
0.721	6.108	3.411	0.002	0.09		0.447	5.441	3.279	-0.043	0.04	
0.721	6.107	3.416	-0.002	0.09		0.721	6.143	3.674	-0.012	0.37	
0.721	6.124	3.462	-0.070	0.09		0.721	6.139	3.654	0.014	0.37	
0.907	5.896	3.714	-0.005	0.16		0.907	5.943	4.065	-0.034	0.1	
0.907	5.888	3.679	0.040	0.16		0.907	5.94	3.985	0.08	0.6	
0.907	5.886	3.671	0.050	0.16		1.107	5.674	4.346	0.019	0.19	
1.107	5.652	4.056	-0.025	0.22		1.107	5.673	4.320	0.046	0.19	
1.107	5.653	4.058	-0.037	0.22		1.401	5.292	4.640	-0.038	0.31	
1.107	5.652	4.060	-0.029	0.22		1.401	5.281	4.636	-0.023	0.37	
1.401	5.283	4.474	-0.002	0.45		Eu(III), phase II $C_A = 10.00$ (mM)					
1.401	5.283	4.476	-0.004	0.45		0.157	6.286	3.570	-0.056	0.05	
1.642	4.997	4.807	-0.048	0.59		0.157	6.286	3.593	-0.069	0.05	
1.642	4.997	4.809	-0.050	0.59		0.321	5.992	3.957	-0.024	0.1	
1.873	4.737	4.982	-0.013	0.79		0.321	5.992	3.965	-0.032	0.10	
1.873	4.737	5.008	-0.039	0.79		0.487	5.687	4.235	-0.001	0.18	
2.276	4.317	5.193	0.012	1.10		0.487	5.687	4.248	-0.012	0.18	
2.276	4.317	5.247	-0.042	1.10		0.721	5.297	4.612	0.017	0.36	
2.573	4.031	5.328	-0.042	1.33		0.721	5.297	4.604	0.025	0.36	
2.573	4.031	5.349	-0.063	1.33		0.907	4.998	5.105	0.035	0.55	
2.924	3.723	6.260	0.004	1.63		0.907	4.998	5.090	0.060	0.55	
2.924	3.723	6.258	-0.002	1.63		1.107	4.699	5.575	0.015	0.76	
Tb(III), phase II $-\log [H^+] = -10$						1.107	4.699	5.552	0.038	0.76	
$C_A \cdot 10^3$ (M)	$-\log [A]$	$-\log S$	$\log \frac{S}{S_{\text{calc}}}$	$\bar{n}$		1.107	4.699	5.552	0.038	0.76	
0.300	3.524	5.745	-0.003	1.81		1.390	4.313	6.622	0.001	1.04	
0.300	3.524	5.762	-0.017	1.81		1.390	4.313	6.616	0.007	1.04	
0.500	3.376	5.843	-0.004	2.39		1.642	4.003	6.629	0.102	1.27	
0.500	3.304	5.819	-0.066	2.39		1.642	4.003	6.625	0.106	1.27	
1.000	3.005	4.954	-0.033	2.40		2.027	3.575	6.737	0.008	1.67	
1.000	1.095	4.965	-0.044	2.40		2.027	3.575	6.723	0.022	1.67	
Tb(III), phase II $C_A = 1.000$ (mM)						2.292	3.302	5.666	-0.007	1.96	
$-\log h$	$-\log [A]$	$-\log S$	$\log \frac{S}{S_{\text{calc}}}$	$\bar{n}$		2.292	3.302	5.695	-0.036	1.96	
0.907	5.568	3.715	0.017	0.14		2.607	3.000	5.483	-0.013	2.19	
0.907	5.565	3.711	0.025	0.14		2.607	3.000	5.417	0.053	2.19	
1.107	5.648	4.143	-0.010	0.22		2.803	2.825	5.272	0.044	2.45	
1.107	5.650	4.165	-0.036	0.22		2.803	2.825	5.247	0.069	2.45	
1.231	5.497	4.400	-0.003	0.29		2.953	2.699	5.149	0.039	2.55	
1.231	5.498	4.428	-0.033	0.29		2.953	2.699	5.13	0.075	2.55	
1.401	5.287	4.743	0.019	0.43		3.184	2.524	5.027	-0.044	2.74	
1.401	5.287	4.746	-0.002	0.43		3.184	2.524	5.076	-0.093	2.74	
1.642	4.999	5.176	0.001	0.59		3.184	2.524	5.073	-0.110	2.74	
1.642	4.999	5.207	-0.030	0.59		Eu(III), phase II $C_A = 10.00$ (mM)					
1.873	4.739	5.520	-0.002	0.79		0.271	6.061	3.944	-0.04	0.99	
1.873	4.739	5.473	0.046	0.79		0.321	5.979	3.59	-0.08	1.1	
2.276	4.318	5.975	-0.009	1.10		0.487	5.692	4.01	0.07	0.18	
2.276	4.318	5.959	0.037	1.10		0.721	5.296	4.72	0.04	0.34	
2.573	4.031	6.165	0.036	1.33		0.721	5.296	4.69	0.07	0.34	
2.573	4.031	6.141	0.050	1.33		0.907	4.998	5.168	0.042	0.55	
2.924	3.722	6.310	-0.042	1.63		0.907	4.998	5.170	0.058	0.55	
2.924	3.722	6.253	0.099	1.63		1.107	4.699	5.614	0.014	0.76	
Tb(III), phase II $C_A = 10.00$ (mM)						1.107	4.699	5.604	0.024	0.76	
1.390	4.313	6.04	-0.07	1.10		1.268	4.474	5.894	-0.006	0.92	
1.390	4.313	6.05	-0.08	1.10		1.268	4.474	5.895	-0.007	0.92	
1.390	4.313	6.05	-0.08	1.10		1.390	4.313	6.052	0.001	1.04	
1.642	4.003	6.16	0.05	1.36		1.390	4.313	6.056	-0.003	1.04	
1.642	4.003	6.14	0.07	1.36		1.620	4.029	6.293	0.003	1.26	
2.027	3.575	6.38	-0.005	1.79		1.620	4.029	6.304	-0.008	1.26	
2.027	3.575	6.38	-0.005	1.79		1.642	4.003	6.346	-0.028	1.27	
2.292	3.302	6.40	-0.001	2.09		1.642	4.003	6.344	-0.030	1.27	
2.292	3.302	6.40	-0.001	2.09		1.770	3.856	6.412	0.001	1.31	
2.607	3.900	6.17	-0.008	2.40		1.770	3.856	6.411	0.002	1.31	
2.607	3.900	6.17	-0.008	2.40		2.026	3.576	6.544	-0.001	1.67	
2.803	2.824	6.12	-0.04	2.57		2.026	3.576	6.531	0.012	1.67	
2.953	2.699	6.19	-0.09	2.68		2.222	3.373	6.627	-0.039	1.89	
3.184	2.524	6.04	0.00	2.81		2.222	3.373	6.644	-0.056	1.89	
3.184	2.524	6.03	0.01	2.81		2.398	3.198	6.593	0.003	2.07	
3.184	2.524	6.05	-0.001	2.81		2.398	3.198	6.587	0.006	2.07	
3.551	2.301	5.84	-0.09	2.98		2.523	3.078	6.611	-0.036	2.20	
3.551	2.301	5.83	0.01	2.98		2.523	3.078	6.611	-0.036	2.20	
3.551	2.301	5.85	-0.01	2.98		2.745	2.875	6.506	0.006	2.42	
						2.745	2.875	6.502	0.010	2.42	
						2.921	2.725	6.434	0.004	2.56	
						2.921	2.725	6.432	0.006	2.56	
						3.222	2.497	6.291	-0.003	2.75	
						3.222	2.497	6.281	-0.007	2.75	
						3.523	2.315	6.140	-0.003	2.90	
						3.523	2.315	6.145	-0.008	2.90	
						4.398	2.058	5.883	-0.003	3.09	
						4.398	2.058	5.885	-0.005	3.09	

Table 6. Continued.

Tb(III), phase II $-\log[H^+] = 6.00$						Eu(III), phase II $-\log[H^+] = 6.00$					
$C_A \cdot 10^3$ (M)	$-\log[A]$	$-\log S$	$\log \frac{S}{S_{calc}}$	$\bar{n}$		$C_A \cdot 10^3$ (M)	$-\log[A]$	$-\log S$	$\log \frac{S}{S_{calc}}$	$\bar{n}$	
0.530	3.373	6.522	-0.08	2.09		1.400	1.885	5.654	-0.010	3.23	
		6.56	0.06			1.400	1.895	5.654	-0.010	3.23	
1.060	3.373	6.536	-0.10	2.40		2.000	1.701	5.394	0.052	3.34	
		6.519	-0.02			2.000	1.701	5.389	0.058	3.34	
1.590	3.373	6.527	0.04	2.57		2.800	1.655	5.232	0.010	3.45	
		6.57				2.800	1.655	5.224	0.018	3.45	
2.120	3.373	6.519	0.05	2.68		3.75	1.428	5.084	-0.001	3.53	
		6.519				3.75	1.428	5.053	-0.002	3.53	
3.00	2.525	6.036	0.005	2.81		5.00	1.303	4.857	-0.000	3.61	
2.20	2.323	5.851	-0.008	2.99		5.00	1.303	4.860	-0.003	3.61	
5.00	2.303	5.862	-0.019	2.99		6.30	1.202	4.692	-0.000	3.67	
13.00	2.002	5.44	0.08	3.18		6.30	1.202	4.688	0.004	3.67	
10.00	2.002	5.38	0.14	3.18							
20.00	1.701	5.55	-0.02	3.18							
20.00	1.701	5.162	-0.078	3.19							
37.5	1.428	4.735	-0.003	3.56							
37.5	1.424	4.741	-0.003	3.56							
50.0	1.103	4.532	0.02	3.69							
50.0	1.113	4.576	0.043	3.61							
75.0	1.120	4.13	0.016	3.77							
75.0	1.120	4.117	0.019	3.72							

Perchloric acid has to be added to the solutions containing the lowest oxalate concentrations and this will cause small variations in the ionic strength of the solutions. The variations are usually small and can be calculated from the data in Tables 5 and 6.

Determination of the phase transition points. The phase transition points have been determined by the following three methods:

a. The point of intersection between the two solubility curves have been determined graphically. The difference in slope between the two curves was in all cases sufficiently large for an accurate determination.

b. Approximately 0.2 g of the phases I and II (or II and III) were added to a solution with an oxalate concentration close to the expected transition point. As equilibrium was approached the relative amounts of the two phases changed. The oxalate concentration of the solution in equilibrium with two solid phases present is equal to $[A]_I$ resp. $[A]_T$ and was determined by a potentiometric determination of the concentration of free hydrogen ions, h , followed by a cerimetric determination of the total oxalate concentration.

c. The phase-transition points can also be calculated from the experimental values of the two solubility products.

Rate of phase transitions. The rate for the transformation phase I $\longrightarrow$ phase II is rather slow, especially in the vicinity of the transition point. The oxalate concentration can usually be increased by a factor two to three above the value at the transition point without any noticeable changes in the composition of the solid during an equilibration time of 1 h. If the oxalate concentration is increased beyond this limit a rapid phase transition occurs. The phase-transition phase II $\longrightarrow$ phase I always proceeds much faster than the reverse transition and for the determination of the solubility when the solid was metastable much shorter equilibration times had to be used. In the cerium and terbium systems the transition II $\longrightarrow$ I occurred so fast that no solubilities of phase II could be determined to the left of the first transition point. The transition phase II $\longrightarrow$ phase III and its reverse are both fairly slow and it is possible to study the meta-stable phases over a large range of oxalate concentrations.

Determination of the protonation constants for the oxalate ion. The protonation constants δ_1 and δ_2 were determined by potentiometric h -determinations in different buffers of oxalic acid and sodium oxalate. The method has been described before.¹ The galvanic elements used were of the type:

Au	C_{H_2A}	1.00 M NaClO ₄	10.00 mM HClO ₄	Au
	C_{Na_2A}		$I = 1.00$ (M)	
	$I = 1.00$ (M)		Quinhydrone	
	Quinhydrone			

Results

Protonation constants of the oxalate ion. The stability constants δ_1 and δ_2 were determined by standard methods (graphical) from the experimental material in Table 2. The following values were obtained:

$$\begin{aligned}\delta_1 &= (3.55 \pm 0.04) \times 10^3 \text{ (M}^{-1}\text{)} \\ \delta_2 &= (3.62 \pm 0.11) \times 10^4 \text{ (M}^{-2}\text{)}\end{aligned}$$

The errors quoted are estimated maximum errors. The acidity constants do not vary with the total buffer concentration in the range investigated (5 mM–100 mM), cf. Table 3.

Values of the various phase-transition points. The experimental values of the different phase-transition points are given in Table 4. The final values are given in the last column of the table and have been obtained by taking into account the results of all the different methods of determination. The two-phase method gives erroneous results for the first transition point in the cerium case — a reason for this might be that some other solid phase is formed in this experiment. In this connection it may be mentioned that $\text{Ce}_2\text{A}_3 \cdot x\text{H}_2\text{O}$ has been reported to contain between nine and twelve water molecules.¹⁴

Solubility measurements. The solubility data for the various phases of the investigated rare earths are collected in Tables 5 and 6, the corresponding solubility curves are shown in Figs. 1 and 2.

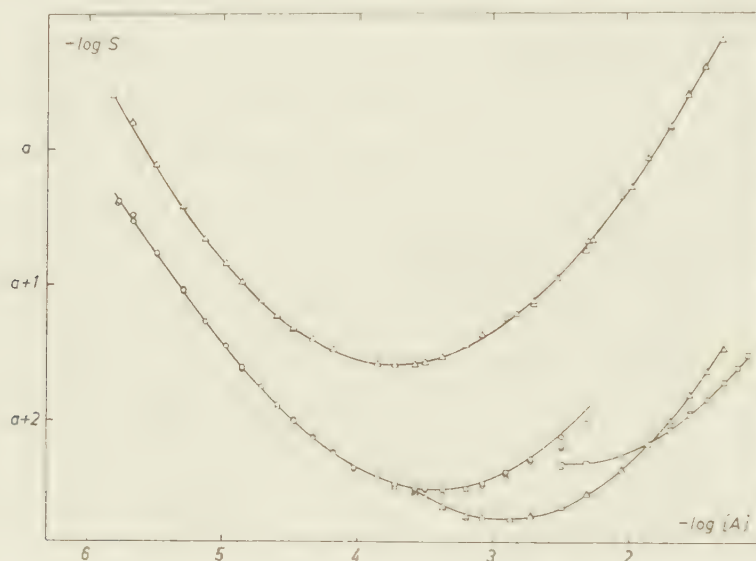


Fig. 1. Experimental solubility curves for the cerium and lutetium oxalate systems. The value of a is equal to 3 for the cerium system (the lower curves) and equal to 4 for the lutetium system (the upper curve). The full-drawn curves have been calculated with the final set of solubility products and stability constants given in Table 8.

In the cerium-oxalate system we could only determine one solubility product directly from solubility measurements at low oxalate concentrations and had to determine the other two from the phase-transition points. A direct determination of the two solubility products was possible for europium and terbium even if the second solubility product is more uncertain than the first. The "best" solubility product was also based on the results obtained from the phase-transition point. For lutetium, $\text{NaLuA}_2 \cdot 4\text{H}_2\text{O}$ was the only stable solid in the oxalate range investigated.

The constants $\beta_{i,j}K^{i/q}$ were determined for each phase and the result is given in Table 7. The errors quoted are equal to three standard deviations. From the different values in Table 7 a final "best" set of stability constants, $\beta_{i,j}$, was chosen and the errors in these constants were estimated from the 3σ -values of Table 7. The final values of the various solubility products and stability constants are given in Table 8.

The full-drawn curves in Figs. 1 and 2 have been calculated using these sets of constants. The agreement between experimental and calculated solubility is satisfactory.

The fact that the different phases for each of the investigated systems give the same stability constants proves that the complexes formed are mononuclear. A maximum of four oxalate groups are coordinated to the various central ions in the oxalate range investigated, and it is not likely that complexes higher than the fourth can be formed in aqueous solution (*vide* the values of $\bar{n}$ for Lu in Table 5).

The possible occurrence of acid complexes must also be investigated. For the europium-oxalate system, we have measured the solubility of phase I in solutions with the same free oxalate concentration but with different

Table 7. Values of the constants $\beta_{i,j}K^{i/q}$ for the various lanthanoide oxalate phases. The errors quoted are equal to three standard deviations.

Constant	Ce(III)	Eu(III)	Tb(III)	Lu(III)
$K_I^{1/2} \times 10^{14} (\text{M}^{1/2})$	88.5 $\pm$ 3.7	10.1 $\pm$ 0.8	24.5 $\pm$ 1.8	
$\beta_1 \cdot K_I^{1/2} \times 10^8 (\text{M}^{7/2})$	2.72 $\pm$ 0.20	1.34 $\pm$ 0.22	2.56 $\pm$ 0.40	
$\beta_2 \cdot K_I^{1/2} \times 10^5 (\text{M}^{1/2})$	7.12 $\pm$ 0.74	5.7 $\pm$ 1.7	18.7 $\pm$ 5.4	
$\beta_3 \cdot K_I^{1/2} \times 10^3 (\text{M}^{-1/2})$	1.24 $\pm$ 0.30	3.7 $\pm$ 1.1	13.5 $\pm$ 8.1	
$K_{II} \times 10^{10} (\text{M}^4)$	138 $\pm$ 10	2.86 $\pm$ 0.30	2.95 $\pm$ 0.72	4.60 $\pm$ 0.36
$\beta_1 \cdot K_{II} \times 10^{11} (\text{M}^3)$	39.4 $\pm$ 2.1	3.19 $\pm$ 0.33	3.45 $\pm$ 1.2	8.85 $\pm$ 0.66
$\beta_2 \cdot K_{II} \times 10^6 (\text{M}^2)$	1.12 $\pm$ 0.05	12.1 $\pm$ 2.1	24.6 $\pm$ 9.6	1.57 $\pm$ 0.12
$\beta_3 \cdot K_{II} \times 10^4 (\text{M})$	2.84 $\pm$ 0.17	1.10 $\pm$ 0.13	2.20 $\pm$ 0.66	25.3 $\pm$ 1.7
$\beta_4 \cdot K_{II} \times 10^3$	7.46 $\pm$ 0.82	3.39 $\pm$ 0.54	7.4 $\pm$ 2.5	222 $\pm$ 10
$K_{III}^{1/2} \times 10^{15} (\text{M}^{11/2})$	1.67 $\pm$ 0.15			
$\beta_3 \cdot K_{III}^{1/2} \times 10^5 (\text{M}^{5/2})$	3.35 $\pm$ 0.25			
$\beta_4 \cdot K_{III}^{1/2} \times 10^4 (\text{M}^{3/2})$	9.7 $\pm$ 1.2			

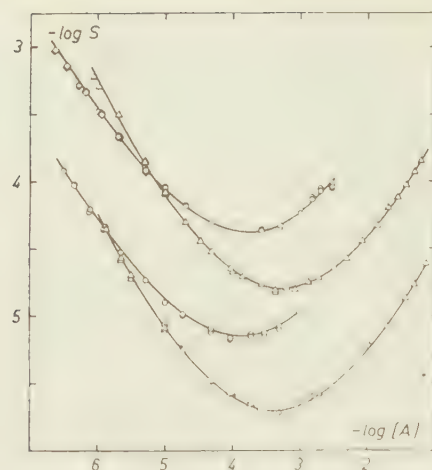


Fig. 2. Experimental solubility curves for the europium and terbium oxalate systems. The upper curve denote the europium system and the lower curve the terbium system. The full-drawn curves have been calculated with the constants in Table 8.

hydrogen ion concentrations. We found that the solubility curve in the range $5.3 < \text{pA} < 6.3$ was independent of the hydrogen-ion concentration and thus conclude that no acid complexes are formed in our range of measurement. This conclusion is supported by the investigation of Sekine.⁸

SOLVENT EXTRACTION MEASUREMENTS

Solvent extraction measurements have only been made for the europium and terbium oxalate systems in order to confirm the presence of a fourth complex. For this reason, we have made the largest part of the experimental distribution measurements at an oxalate range where the highest complexes

Table 8. Final solubility products and stability constants for the investigated lanthanoide oxalate systems with their estimated maximum errors. The ratio between the various stepwise stability constants are also given.

Constant	Ce(III)	Eu(III)	Tb(III)	Lu(III)
$K_I \times 10^{26} (M^5)$	78 $\pm$ 5	1.17 $\pm$ 0.15	5.9 $\pm$ 0.7	
$K_{II} \times 10^{16} (M^4)$	138 $\pm$ 10	2.8 $\pm$ 0.3	2.9 $\pm$ 0.3	4.60 $\pm$ 0.05
$K_{III} \times 10^{30} (M^{11})$	2.8 $\pm$ 0.5			
$\beta_1 \times 10^{-4} (M^{-1})$	3.1 $\pm$ 0.3	11.0 $\pm$ 1.5	12.0 $\pm$ 2.0	19.0 $\pm$ 1.0
$\beta_2 \times 10^{-8} (M^{-2})$	0.81 $\pm$ 0.10	5.0 $\pm$ 0.7	7.2 $\pm$ 1.7	34 $\pm$ 2
$\beta_3 \times 10^{-11} (M^{-3})$	0.20 $\pm$ 0.02	3.7 $\pm$ 0.6	7.1 $\pm$ 1.5	55 $\pm$ 3
$\beta_4 \times 10^{-13} (M^{-4})$	0.56 $\pm$ 0.06	12.4 $\pm$ 1.6	26 $\pm$ 6	480 $\pm$ 30
K_1/K_2	12 $\pm$ 2	24 $\pm$ 6	20 $\pm$ 6	11 $\pm$ 2
K_2/K_3	11 $\pm$ 2	6 $\pm$ 4	6 $\pm$ 4	11 $\pm$ 2
K_3/K_4	9 $\pm$ 2	22 $\pm$ 8	27 $\pm$ 10	18 $\pm$ 4

are present in largest amounts. The experimental method used is the same as described by Sekine⁸ using TTA and hexone as extracting agents and carbon tetrachloride as the solvent.

Notations. The general equations used have been given by Sekine. The function X can be determined from measurements of the distribution of metal between organic and aqueous phase and

$$X = D_0/D \quad (12)$$

where D_0 is the distribution coefficient when $C_A=0$. The following expression may be derived from eqn. (12)

$$\frac{d \log D^{-1}}{d \log [A]} = \bar{n} \quad (13)$$

Experimental

Chemicals used. TTA (Columbia Organic Chemical Co) was used without further purification. Hexone (Merck) and carbon tetrachloride (Merck) were both of analytical grade. All other solutions were the same as described in the preceding section.

Distribution measurements. The experimental conditions had to be optimized in order to get as accurate distribution coefficients as possible ($-2 < \log D < 2$). Since the value of D is dependent on the hydrogen-ion concentration it was practical to keep h as constant as possible. The hydrogen ion concentration had to be rather low ($-\log h > 4.0$) in order to prevent precipitation of NaHA at the high oxalate concentrations used in this investigation. The hydrogen-ion concentration changed slightly during the equilibration with the organic phase and was therefore measured with a Radiometer PhM 4 c pH-meter. All the measured distribution coefficients were then recalculated to a "normalized" hydrogen-ion concentration equal to $10^{-4.564}$ M, and were then denoted D .

The distribution coefficients were determined in the following way: 5.00 ml of a ligand solution and 0.0500–0.300 ml of a radioactive rare-earth solution were equilibrated with 5.00 ml of an organic phase containing 0.400 M TTA and ten volume percent hexone. Equilibrium was attained by agitation for two hours at 20.0°C. The total lanthanoid concentration in the two phases was then determined by γ -activity measurements as described before (p. 98). The total metal concentration in the aqueous phase was in all cases so low that no rare earth oxalate could precipitate.

Results

The experimental values of D are given in Table 9 and have been plotted in Fig. 3 as $(\log D^{-1} + \text{const})$ versus pA. The slope of this curve is equal to $\bar{n}$ and it is obvious from the figure that the slope is larger than three at the highest oxalate concentrations. The fact that more than three complexes are formed is more obvious from Fig. 4 where we have used the relation:

$$\frac{1}{D[A]^4} = \frac{\beta_4}{D_0} + \frac{\beta_3}{D_0} \cdot \frac{1}{[A]} + \dots$$

and plotted $1/D[A]^4$ versus $1/[A]$. The result is a straight line from which a value of K_4 can be determined. The following values were obtained for the two systems investigated:

extr.	Eu(III) $K_4 = 39 \pm 4$ (M ⁻¹)	sol.	$K_4 = 34 \pm 5$ (M ⁻¹)
	Tb(III) $K_4 = 41 \pm 5$ (M ⁻¹)		$K_4 = 37 \pm 10$ (M ⁻¹)

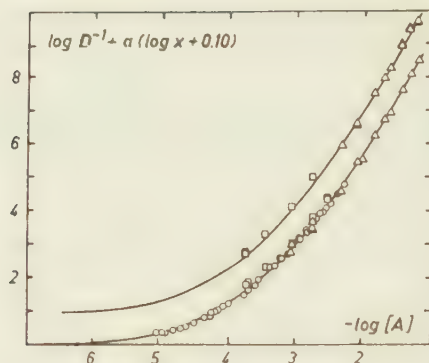


Fig. 3. $\log D^{-1} + \text{const}$ as a function of $-\log [A]$ for the europium and terbium oxalate system. a equals 5.68 for the europium system (the lower curve) and 6.91 for the terbium system. The full-drawn curves have been calculated from the values of $\log X$ obtained from the solubility measurements. The circles denote the values of $(\log X + 0.10)$ where $\log X$ have been determined by Sekine.⁶

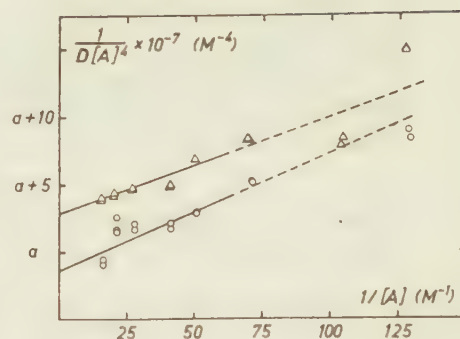


Fig. 4. Graphical evaluation of the constant K_4 from solvent-extraction data for the europium and terbium oxalate systems. The lower curve refers to the terbium system where the value of a equals 5 and the upper curve to the europium system where a equals 0.

These results are in good agreement with the values found from the solubility data.

We did not make any attempt to determine D_0 experimentally. This constant was calculated from eqn. (12) and the values of X obtained from the solubility data instead. The full-drawn curves in Fig. 3 have been calculated using the final constants given in Table 8. The extraction data are well described by this curve and we have thus confirmed the existence of a fourth complex and also the value of the fourth consecutive stability constant.

For the europium-oxalate system, we could directly compare our results with those of Sekine. His $\log X$ -values are systematically lower than ours. We have therefore in Fig. 3 added 0.10 to Sekine's $\log X$ -values and denoted the result with circles. One can now notice a good agreement between the two sets of extraction data and the values of $\log X$ -obtained from the solubility measurements. The systematic displacement might be caused by a systematic error in the determination of D_0 . Some support for this conclusion is given by the fact that a plot of Sekine's values of $(X - \beta_3[A]^3)$ versus $[A]$ gives an extrapolated value of $X = 0.8 \pm 0.2$ when $[A] = 0$, i.e. his value of $\log D_0$ should be increased with approximately 0.10 units.

DISCUSSION

This investigation has shown that the lanthanoid ions form stable mononuclear oxalate complexes in solution. A maximum of four oxalate groups are coordinated to the central ion probably forming a complex with a coordina-

Table 9. Corresponding values of $-\log [A]$, $-\log h$, $\log D^{-1}$ and $\log D^{-1}$ for the europium and terbium oxalate systems.

$-\log [A]$	$-\log h$	$\log D^{-1}$	$\log D^{-1}$	$-\log [A]$	$-\log h$	$\log D^{-1}$	$\log D^{-1}$
3.737	3.442	-1.767	-3.91	3.768	3.388	-1.286	-4.18
3.709	3.493	-1.250	-3.83	3.769	3.386	-1.230	-4.13
3.441	3.503	-0.822	-3.38	3.479	3.434	-0.852	-3.61
3.441	3.503	-0.814	-3.37	3.480	3.430	-0.836	-3.61
3.062	3.464	-0.023	-2.69	3.083	3.424	0.001	-2.79
3.055	3.478	-0.039	-2.67	3.083	3.424	0.005	-2.79
2.760	3.507	0.652	-1.89	2.769	3.486	0.685	-1.92
2.760	3.507	0.660	-1.88	2.769	3.486	0.690	-1.92
2.544	3.510	1.210	-1.32	2.330	4.207	-0.516	-0.96
2.540	3.519	1.158	-1.35	2.111	4.233	0.044	-0.32
3.081	3.975	-1.803	-2.94	2.109	4.248	0.028	-0.29
3.081	3.975	-1.800	-2.94	1.852	4.287	0.798	0.60
3.068	4.026	-1.730	-2.71	1.850	4.292	0.792	0.61
2.774	3.995	-1.179	-2.26	1.704	4.321	1.173	1.08
2.768	4.021	-1.226	-2.23	1.704	4.316	1.192	1.08
2.755	4.073	-1.209	-2.05	1.616	4.336	1.419	1.37
2.337	4.170	-0.582	-1.13	1.616	4.334	1.448	1.39
2.337	4.170	-0.578	-1.13	1.446	4.345	2.063	2.04
2.105	4.271	0.002	-0.25	1.445	4.353	2.073	2.07
2.105	4.271	0.005	-0.25	1.328	4.354	2.496	2.50
2.019	4.262	0.122	-0.16	1.328	4.353	2.513	2.51
2.015	4.285	0.041	-0.17	1.329	4.349	2.578	2.56
1.844	4.307	0.684	0.54	1.214	4.358	2.737	2.75
1.841	4.327	0.639	0.56	1.214	4.361	2.770	2.79
1.700	4.320	1.139	1.04				
1.698	4.330	1.117	1.05				
1.612	4.320	1.341	1.24				
1.612	4.320	1.349	1.25				
1.434	4.344	1.964	1.93				
1.434	4.344	1.967	1.93				
1.310	4.337	2.432	2.38				
1.310	4.337	2.452	2.40				
1.193	4.354	2.812	2.81				
1.193	4.354	2.830	2.83				

tion number of at least eight. Such a high coordination number is not unexpected¹⁵ because of the high charge and fairly large ionic radius of the lanthanoid elements.

From the variations of the stepwise stability constants, *cf.* Table 8, one can see that there is no difficulty for the fourth complex to be formed. This fact indicates that the steric effects noticed previously for the oxydiacetato and 2,6-pyridinodicarboxylato ligands, to the largest part are caused by the geometrical requirements of the ligands.

The results of this investigation are also supported by the work of Sekine.⁸ The results of the earlier solubility measurements⁴⁻⁶ are probably more or less in error.

Acknowledgements. This investigation has in part been supported by a grant from *Statens Naturvetenskapliga Forskningsråd* (Swedish Natural Science Research Council).

Acta Chem. Scand. 23 (1969) No. 1

REFERENCES

1. Grenthe, I. and Tobiasson, I. *Acta Chem. Scand.* **17** (1963) 2101.
2. Grenthe, I. *J. Am. Chem. Soc.* **83** (1961) 360.
3. Cotton, A., Ed., *Progress in Inorganic Chemistry*, Interscience 1967, Vol. 8, p. 109.
4. Crouthamel, C. E. and Martin, D. S., Jr. *J. Am. Chem. Soc.* **72** (1950) 1382.
5. Crouthamel, C. E. and Martin, D. S., Jr. *J. Am. Chem. Soc.* **73** (1951) 569.
6. Feibush, A. M., Rowley, K. and Gordon, L. *Anal. Chem.* **30** (1958) 1610.
7. Zaborenko, K. B., Zaval'skaya, A. V. and Fomin, V. V. *Radiokhimiya* **1** (1959) 387.
8. Sekine, T. *Acta Chem. Scand.* **19** (1965) 1476.
9. Rossotti, F. J. C. and Rossotti, H. *The Determination of Stability Constants*, McGraw, New York, Toronto, London 1961.
10. Grenthe, I. *Acta Chem. Scand.* **16** (1962) 1695.
11. Grenthe, I. and Williams, D. R. *Acta Chem. Scand.* **21** (1967) 341.
12. Hansson, E. and Albertsson, J. *Acta Chem. Scand.* **22** (1968) 1682.
13. Ahrland, S. and Johansson, L. *Acta Chem. Scand.* **18** (1964) 2125.
14. Gmelin-Kraut, *Handbuch der anorganischen Chemie*, Heidelberg 1932, Band VI, Abteilung 2, p. 223.
15. Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, Ithaca, New York 1969, p. 220.

Received June 5, 1968.

Ref. B

Thermodynamic Properties of Rare Earth Complexes

VIII. Stability Constants for Oxalate Complexes of Sc(III)

GÖRAN GÄRDHAMMAR

*Division of Physical Chemistry, Chemical Center, University of Lund,
P.O.B. 740, S-220 07 Lund 7, Sweden*

The stability constants for the formation of four mononuclear scandium(III) oxalato complexes have been determined at 20°C in an aqueous sodium perchlorate medium with ionic strength 1 M. Three different methods were used, viz. solvent extraction with thenoyltrifluoroacetone as the auxiliary ligand, solubility measurements by using $\text{Na}_3\text{Sc}(\text{C}_2\text{O}_4)_3 \cdot x \text{H}_2\text{O}$ as the solid phase, and potentiometric measurements of the hydrogen ion concentration.

The chemical properties of scandium(III) are very similar to those of the trivalent lanthanoids. A comparison of the values of ΔG_i° , ΔH_i° and ΔS_i° for the formation of some scandium(III) and lanthanoid(III) complexes has previously been published in this series.¹ The differences between the complexes could be discussed in terms of the ionic radius of the central ion and the special geometrical requirements of the ligand used. This investigation is an extension of the previous study to include the ligand oxalate.

The complex formation between oxalate and some lanthanoid(III) ions (Ce, Eu, Tb, and Lu) has previously been studied (Part VI in this series²), mainly by solubility measurements. Only a few incomplete investigations of scandium oxalato complexes have been published so far. These include two spectrophotometric studies,^{3,4} one solvent extraction study using oxine (8-hydroxyquinoline) as auxiliary ligand⁵ and one ion-exchange investigation.⁶ In one of the spectrophotometric studies³ only the complex ScA^+ (A denotes oxalate) was studied, while in the other⁴ the presence of three complexes ScA_j^{3-2j} ($j=1-3$) was reported. The results of the latter investigation are doubtful, because the range of oxalate concentration investigated was very narrow (3×10^{-5} M to 1.4×10^{-4} M). The solvent extraction study took only the complex ScA_3^{3-} into account. The ion-exchange study is also incomplete, as no information about complexes higher than ScA_2^- was obtained.

In the present study three different methods have been used. All measurements have been performed in a medium with ionic strength 1 M, using sodium perchlorate as the inert electrolyte. The temperature was 20°C. The protona-

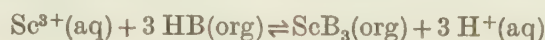
tion constants of oxalic acid in this medium and at this temperature have been determined before (Part VI, p. 102). The symbols not defined below have been given in Part I in this series.⁷ ($[H^+]$ in Ref. 7 is here replaced with h .)

SOLVENT EXTRACTION MEASUREMENTS

The distribution of scandium(III) between an organic and an aqueous phase was studied by using xylene as the organic solvent and thenoyltrifluoroacetone (TTA) as the extracting agent. The aqueous phase consisted of solutions with different oxalate concentrations and with ionic strength 1.00 M.

Calculations

The distribution equilibrium can be written



with an equilibrium constant equal to K_{ex} . The distribution ratio, D , of Sc(III) between the two phases is equal to

$$D = \frac{[\text{ScB}_3]_{\text{org}}}{[\text{Sc}^{3+}] \cdot X} \quad (1)$$

if the only scandium complexes in the aqueous phase have the composition $\text{ScA}_i\text{H}_k^{3-2i}$, and the only species in the organic phase can be represented by $\text{ScB}_3(\text{Xylene})_n$. The existence of species of the type $\text{Sc}_i\text{A}_j\text{H}_k^{3i+k-2j}$ ($i > 1$, $k \neq 0$) are discussed below (*vide infra* p. 167). The complex formation between scandium and the auxiliary ligand is probably of little importance in the aqueous phase.⁸

The corresponding distribution ratio when no oxalate is present is given by

$$D_0 = \frac{[\text{ScB}_3]_{\text{org}}}{[\text{Sc}^{3+}]} = \frac{K_{\text{HB}}}{h^3} \quad (2)$$

where $K_{\text{HB}} = K_{\text{ex}} \cdot [\text{HB}]_{\text{org}}^3 \cdot f_{\text{HB}}^3 \cdot f_{\text{ScB}_3}^{-1}$. Here f_{HB} and f_{ScB_3} are the activity coefficients for the species HB and ScB_3 in the organic phase.

In the present case the volume ratio between the two phases is constant. The total concentration of scandium is very small compared with the initial concentration of auxiliary ligand, $[\text{HB}]_{\text{org}}'$. When $[\text{HB}]_{\text{org}}'$ is kept constant, $[\text{HB}]_{\text{org}}$ (the equilibrium concentration) and K_{HB} are constant.⁹⁻¹¹ K_{HB} can be determined by distribution measurements with $C_A = 0$ and with $[\text{HB}]_{\text{org}}'$ kept constant; cf. eqn. (2).

The function X is calculated from corresponding values of D , K_{HB} , and h :

$$X = \frac{D_0}{D} = \frac{K_{\text{HB}}}{h^3 \cdot D} \quad (3)$$

Experimental

Chemicals. A stock solution of scandium perchlorate was prepared by dissolving scandium oxide (Johnson, Matthey & Co.; 99.99 %) in warm perchloric acid (Baker's Analysed). A 0.2 M solution was prepared and analysed for scandium with EDTA using xylenolorange as an indicator. The concentration of free hydrogen ions, which was determined potentiometrically, was kept as high as 0.4 M in order to avoid hydrolysis.^{12,13} Stock solutions of sodium perchlorate were prepared and analysed as described earlier.¹⁴ Stock solutions of oxalic acid and sodium oxalate (both Merck *p.a.*) were analysed as before.² TTA (Baker's Analysed) was used as received. Xylene was of analytical grade with a boiling range of 138–139°C. The radioactive tracer (⁴⁶Sc) was obtained from New England Nuclear Corp. A radioactive stock solution of scandium perchlorate in water was prepared by mixing the inactive solution of scandium perchlorate with the original ⁴⁶Sc solution.

Distribution measurements. Radioactive scandium solutions in xylene were prepared by extraction from the active water stock solution into the organic TTA-phase. Three different concentrations of TTA (0.400 M, 0.698 M, and 1.400 M) were used. The scandium concentration in these organic stock solutions ranged between 2×10^{-6} M and 1×10^{-6} M. Equal volumes (5 ml) of an active organic phase and an aqueous phase containing oxalate were then agitated vigorously for 2 h at $20 \pm 1^\circ\text{C}$. The compositions of the oxalate solutions are given in Table 2. Equilibrium was attained in less than 30 min. The phases were separated by centrifugation, and the distribution value, D , was determined by γ -activity measurements ^{2,p.6} on 3 ml samples of the two phases.

Results

Determination of K_{HB} -values. Values of K_{HB} were obtained from eqn. (2) from the experimental data of D_0 and h given in Table 1. K_{HB} was equal to $(8.17 \pm 0.46) \times 10^{-3} \text{ M}^3$, $(3.98 \pm 0.15) \times 10^{-2} \text{ M}^3$, and $0.291 \pm 0.008 \text{ M}^3$ for TTA

Table 1. The determination of different K_{HB} from eqn. (4). Every K_{HB} represents one separately determined distribution.

I.	[HB] _{org} ' = 0.400 M. $h = 0.1225 \text{ M}$: $K_{\text{HB}} \times 10^3/\text{M}^3 = 758, 855, 733, 782$. $h = 0.245 \text{ M}$: $K_{\text{HB}} \times 10^3/\text{M}^3 = 800, 794, 877, 789, 798, 799, 822, 890, 779$. $h = 0.493 \text{ M}$: $K_{\text{HB}} \times 10^3/\text{M}^3 = 794, 820, 749, 881, 887, 861, 842, 847$.
II.	[HB] _{org} ' = 0.698 M. $h = 0.245 \text{ M}$: $K_{\text{HB}} \times 10^4/\text{M}^3 = 386, 376, 398, 386$. $h = 0.493 \text{ M}$: $K_{\text{HB}} \times 10^4/\text{M}^3 = 382, 405, 422, 410$. $h = 0.986 \text{ M}$: $K_{\text{HB}} \times 10^4/\text{M}^3 = 398, 418$.
III.	[HB] _{org} ' = 1.400 M. $h = 0.493 \text{ M}$: $K_{\text{HB}} \times 10^3/\text{M}^3 = 291, 290, 277$. $h = 0.739 \text{ M}$: $K_{\text{HB}} \times 10^3/\text{M}^3 = 291, 294$. $h = 0.986 \text{ M}$: $K_{\text{HB}} \times 10^3/\text{M}^3 = 303, 282, 299$.

concentrations equal to 0.400 M, 0.698 M, and 1.400 M, respectively. The errors quoted are equal to the standard deviation of the means.

Determination of stability constants. Experimental values of D and X are given in Table 2, and a plot $\lg X$ versus $\lg([A]/M)$ is shown in Fig. 1. The stability constants were obtained by the graphical standard methods of Leden and Fronæus.¹⁵ The values were then refined by a least squares method.

Table 2. Experimental values from the solvent extraction measurements.

$\frac{[\text{HB}]_{\text{org}}'}{\text{M}}$	$-\lg \frac{[\text{A}]}{\text{M}}$	$-\lg \frac{h}{\text{M}}$	$\lg D$	$\lg X$	$\lg \frac{X}{X_{\text{calc}}}$
1.4	7.585	0.006	-0.627	0.109	-0.024
1.4	7.585	0.006	-0.650	0.132	-0.001
1.4	7.585	0.006	-0.668	0.150	0.017
1.4	7.347	0.131	-0.340	0.198	-0.013
1.4	7.347	0.131	-0.337	0.196	-0.015
0.7	7.199	0.210	-1.055	0.286	0.010
0.7	7.199	0.210	-1.053	0.284	0.008
0.7	7.020	0.307	-0.856	0.377	0.005
0.7	7.020	0.307	-0.862	0.384	0.012
0.7	6.790	0.434	-0.650	0.551	0.026
0.7	6.790	0.434	-0.633	0.535	0.010
0.7	6.790	0.434	-0.622	0.524	-0.001
0.7	6.648	0.514	-0.529	0.672	0.036
0.7	6.648	0.514	-0.521	0.665	0.029
0.7	6.480	0.611	-0.348	0.780	-0.003
0.7	6.480	0.611	-0.351	0.783	0.000
0.7	6.272	0.735	-0.201	1.005	0.017
0.7	6.272	0.735	-0.206	1.011	0.023
0.7	5.990	0.910	0.011	1.320	0.016
0.7	5.990	0.910	-0.007	1.337	0.033
0.7	5.990	0.910	0.011	1.320	0.016
1.4	5.750	0.460	-0.749	1.592	-0.020
1.4	5.750	0.460	-0.733	1.576	-0.036
1.4	5.750	0.460	-0.773	1.616	0.004
0.7	5.553	1.208	0.306	1.919	0.028
0.7	5.553	1.208	0.300	1.924	0.033
1.4	5.500	0.603	-0.648	1.924	-0.047
1.4	5.500	0.603	-0.673	1.948	-0.023
1.4	5.500	0.603	-0.709	1.984	0.013
0.7	5.267	1.424	0.562	2.308	-0.033
0.7	5.267	1.424	0.573	2.297	-0.044
1.4	5.250	0.752	-0.674	2.395	0.026
1.4	5.250	0.752	-0.672	2.393	0.024
1.4	5.250	0.752	-0.670	2.391	0.022
0.7	5.058	1.593	0.707	2.674	-0.024
0.7	5.058	1.593	0.669	2.711	0.013
1.4	5.000	0.908	-0.640	2.829	0.028
1.4	5.000	0.908	-0.627	2.816	0.015
1.4	4.750	1.074	-0.583	3.268	0.008
1.4	4.750	1.074	-0.578	3.264	0.004
0.7	4.750	1.074	-1.417	3.238	-0.022
0.7	4.750	1.074	-1.425	3.246	-0.014
0.7	4.729	1.881	0.942	3.301	0.001
0.7	4.729	1.881	0.947	3.295	-0.005
1.4	4.500	1.251	-0.538	3.755	0.016
1.4	4.500	1.251	-0.539	3.756	0.017
0.7	4.500	1.251	-1.378	3.731	-0.008
0.7	4.500	1.251	-1.374	3.726	-0.013
0.7	4.445	2.149	1.191	3.854	0.007
0.7	4.445	2.149	1.206	3.840	-0.007
0.7	4.250	1.442	-1.277	4.205	-0.029
0.7	4.250	1.442	-1.304	4.232	-0.002
0.7	4.250	1.442	-1.293	4.220	-0.014

Table 2. Continued.

0.7	4.205	2.388	1.410	4.354	0.030
0.7	4.205	2.388	1.423	4.340	0.016
0.7	4.000	1.648	-1.191	4.734	-0.008
0.7	4.000	1.648	-1.194	4.738	-0.004
0.7	4.000	1.648	-1.202	4.746	0.004
0.7	3.750	1.868	-1.065	5.269	0.003
0.7	3.750	1.868	-1.074	5.278	0.012
0.7	3.500	2.101	-0.915	5.819	0.007
0.7	3.500	2.101	-0.918	5.822	0.010
0.7	3.250	2.349	-0.744	6.389	0.003
0.7	3.250	2.349	-0.727	6.373	-0.013
0.4	3.250	2.349	-1.444	6.401	0.015
0.7	3.000	2.611	-0.559	6.992	-0.004
0.7	3.000	2.611	-0.573	7.005	0.009
0.4	3.000	2.611	-1.255	7.000	0.004
0.4	3.000	2.611	-1.237	6.982	-0.014
0.4	3.000	2.611	-1.209	7.045	0.049
0.4	2.750	2.895	-1.046	7.643	-0.005
0.4	2.750	2.895	-1.039	7.637	-0.011
0.4	2.500	3.223	-0.661	8.243	-0.101
0.4	2.500	3.223	-0.640	8.221	-0.123
0.4	2.250	3.668	-0.186	9.101	0.019
0.4	2.250	3.668	-0.181	9.096	0.014
0.4	2.000	4.000	0.035	9.877	0.014
0.4	2.000	4.000	0.035	9.877	0.014
0.4	1.750	4.000	-0.762	10.674	-0.012
0.4	1.750	4.000	-0.740	10.652	-0.034
0.4	1.750	4.000	-0.753	10.666	-0.020
0.4	1.500	4.000	-1.559	11.471	-0.081
0.4	1.500	4.000	-1.542	11.453	-0.099
0.7	1.500	4.000	-0.840	11.439	-0.113
0.7	1.500	4.000	-0.842	11.442	-0.110
0.7	1.250	4.000	-1.721	12.320	-0.138
0.7	1.250	4.000	-1.714	12.314	-0.144

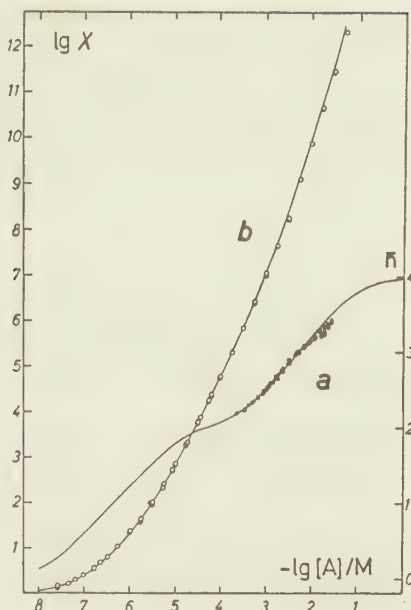
The various constants are given in Table 5. One check of the validity of eqn. (3) was made by measuring D at such low $[A]$ -values that an accurate extrapolation of the X versus $[A]$ curve to $[A]=0$ could be made. The extrapolated value was equal to 0.98 ± 0.04 , in good agreement with the expected value of unity. (The error is an estimated maximum error.)

SOLUBILITY MEASUREMENTS

Scandium(III) forms sparingly soluble oxalates of the general formula $N_p\text{Sc}_q\text{A}_r \cdot x\text{H}_2\text{O}$ (cf. Ref. 2). $N=\text{Na}$, K , or NH_4 . For $N=\text{Na}$, the three following compounds have been described: $\text{Sc}_2\text{A}_3 \cdot x\text{H}_2\text{O}$, $\text{NaScA}_3 \cdot x\text{H}_2\text{O}$, and $\text{Na}_3\text{ScA}_3 \cdot x\text{H}_2\text{O}$.¹⁶ The existence of $\text{Na}_4\text{Sc}_2\text{A}_5 \cdot x\text{H}_2\text{O}$ is doubtful.¹⁶ The various phases are stable in different oxalate concentration ranges, viz. Sc_2A_3 at the lowest and Na_3ScA_3 at the highest.

In the lanthanoid oxalate study,² solubility data from more than one solid phase were obtained. This method was tried in the present study too. However, it was only possible to get reliable results from the solid Na_3ScA_3 .

Fig. 1. *a.* The $\bar{n}$ -curve as a function of $-\lg([A]/M)$ calculated from the final set of constants given in Table 5. The filled circles represent $\bar{n}$ -values from the potentiometric measurements. *b.* The corresponding X - and $-\lg([A]/M)$ -values from the extraction measurements (open circles). The full-drawn curve has been calculated from the final set of constants in Table 5.



Calculations

The calculation of stability constants from solubility data has been given before.^{2,p.95} If only complexes of the type ScA_j^{3-2j} are formed, and the sodium ion concentration is kept constant, the solubility of Na_3ScA_3 is equal to

$$S = K_{\text{III}} \cdot [\text{A}]^{-3} \cdot \sum_{j=0}^J \beta_j \cdot [\text{A}]^j \quad (4)$$

where $K_{\text{III}} = K_{\text{III}} \times [\text{Na}]^{-3}$; K_{III} is the solubility product of Na_3ScA_3 .

If the solubility products of Sc_2A_3 and NaScA_2 are denoted K_{I} and K_{II} , the following relationships will be obtained:

$$K_{\text{I}} = K_{\text{II}}^2 [\text{A}]_{\text{t}}^{-1} \quad (5)$$

and

$$K_{\text{II}} = K_{\text{III}} [\text{A}]_{\text{T}}^{-1} \quad (6)$$

$K_{\text{II}} = K_{\text{III}} [\text{Na}]^{-1}$; $[\text{A}]_{\text{t}}$ and $[\text{A}]_{\text{T}}$ are the oxalate concentrations at the two phase-transition points (cf. Ref. 2).

Experimental

Chemicals. The compound Na_3ScA_3 was obtained from stock solutions of NaClO_4 , $\text{Na}_2\text{C}_2\text{O}_4$, and $\text{Sc}(\text{ClO}_4)_3$ with $[\text{Na}] = 1.00 \text{ M}$ at equilibrium. The free oxalate concentration was kept higher than about 10^{-3} M all the time to avoid the formation of the solids Sc_2A_3 and NaScA_2 . The compound NaScA_2 was prepared as described above, except that the free oxalate concentration was kept between 10^{-5} M and 10^{-4} M . Sc_2A_3 was obtained from $\text{Sc}(\text{ClO}_4)_3$ - and $\text{H}_2\text{C}_2\text{O}_4$ -solutions. The radioactive salts were prepared from Sc-solutions

of known specific activity. The stock solutions and the tracer were the same as described in the previous section.

Analyses of the solid phases. The solids were analysed for scandium and oxalate. The scandium content was determined by oxidation with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ followed by titration with EDTA, while the oxalate content was determined as described before.² The results of the analyses are collected in Table 3.

Table 3. Analyses of the solid phases.

Solid phase	Scandium, %		Oxalate, %		Mol oxalate/ mol Sc (exp.)
	Exp.	Calc.	Exp.	Calc.	
$\text{Sc}_2\text{A}_3 \cdot 11.6 \text{ H}_2\text{O}$	16.01	15.97	46.9	46.9	1.50
$\text{NaScA}_3 \cdot 3.4 \text{ H}_2\text{O}$	14.75	14.73	57.8	57.7	2.00
$\text{Na}_3\text{ScA}_3 \cdot 5.7 \text{ H}_2\text{O}$	9.38	9.35	54.5	54.9	2.97

Solubility measurements. The methods have been described in a previous paper.^{1,p.22} The temperature was $20.0 \pm 0.1^\circ\text{C}$. The various oxalate buffer solutions were prepared as in Ref. 2, with the sodium ion concentration constant = 1.00 M. The compositions of the solutions are given in Table 4.

Table 4. The solubility measurements. h' and C_A' denote concentration values before any solid phase was added. $[A]$ and S are equilibrium values.

h' varying, $C_A' = 9.92 \text{ mM}$

$-\lg(h'/M)$, $-\lg([A]/M)$, $-\lg(S/M)$: 2.611, 2.985, 3.135; 2.611, 2.985, 3.129; 2.611, 2.985, 3.131; 2.895, 2.742, 3.223; 2.895, 2.742, 3.225; 2.895, 2.742, 3.223; 3.223, 2.497, 3.278; 3.223, 2.497, 3.283; 3.223, 2.497, 3.272; 3.668, 2.251, 3.286; 3.668, 2.251, 3.279; 3.668, 2.251, 3.283.

C_A' varying, $\lg(h'/M) = -3.000$

$C_A' \cdot \text{mM}^{-1}$, $-\lg([A]/M)$, $-\lg(S/M)$: 6.37, 2.841, 3.194; 6.37, 2.841, 3.188; 10.19, 2.648, 3.244; 10.19, 2.648, 3.257; 22.6, 2.307, 3.287; 22.6, 2.307, 3.282; 36.9, 2.095, 3.267; 36.9, 2.095, 3.270.

C_A' varying, $\lg(h'/M) = -4.000$

$C_A' \cdot \text{mM}^{-1}$, $-\lg([A]/M)$, $-\lg(S/M)$: 13.55, 2.004, 3.260; 13.55, 2.004, 3.267; 13.55, 2.004, 3.256; 19.73, 1.841, 3.197; 19.73, 1.841, 3.195; 24.1, 1.755, 3.174; 24.1, 1.755, 3.185; 24.1, 1.755, 3.180; 28.4, 1.683, 3.140; 28.4, 1.683, 3.151; 42.8, 1.505, 3.069; 42.8, 1.505, 3.068; 42.8, 1.505, 3.064; 57.1, 1.380, 2.997; 57.1, 1.380, 2.987; 76.2, 1.255, 2.911; 76.2, 1.255, 2.899; 76.2, 1.255, 2.898.

The solubility of Na_3ScA_3 was determined by the column method. The solubility equilibrium was established after only one passage of solution. The solubility was no longer constant when $[A]$ was below about 10^{-3} M and decreased after every passage through the column. A phase-transition probably occurs here.

It was not possible to get any reproducible solubility values for the other two phases, either by using the column method or the agitation method. For the solid Sc_2A_3 some attempts were made to study the solubility in oxalate solutions where no sodium perchlorate had been added. These solutions were about 1.00 M in respect of HClO_4 . The reproducibility was poor here, too. The only possible explanations for this lack of repro-

ducibility seems to be either a very long time of equilibration or some changes in the solid phase.

Determination of the phase-transition points. The method has been described before.^{2,p.101} (Method b. was used.)

Rate of phase-transitions. The rates for the two phase-transformations are very slow; an agitation time of about four weeks is not sufficient to attain complete equilibrium (cf. Ref. 2, p. 101). Because of this, the determinations of the phase-transition points are rather uncertain, but can nevertheless be used for a rough estimation of the solubility products for the solids Sc_2A_3 and NaScA_3 .

Results

Values of the phase-transition points. The concentration of oxalate ions at the transformations $\text{Sc}_2\text{A}_3 \rightarrow \text{NaScA}_2$ and $\text{NaScA}_2 \rightarrow \text{Na}_3\text{ScA}_3$ are equal to $(8 \pm 1) \times 10^{-6}$ M and $(8 \pm 1) \times 10^{-4}$ M, respectively. (The errors are estimated maximum errors.)

Solubility measurements. The solubility data for the solid Na_3ScA_3 are collected in Table 4. The corresponding solubility curve is shown in Fig. 2.

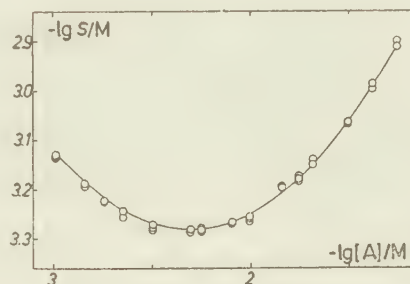


Fig. 2. Experimental values of the solubility for the solid Na_3ScA_3 . The full-drawn curve has been calculated with the final set of solubility product (K_{III}) and stability constants given in Table 5.

The constants $\beta_j K_{\text{III}}$ were determined in a similar way, as described in the extraction part. The results are given in Table 5. As the measurements were restricted to rather high $[A]$ -values, only the constants with $j = 2 - 4$ could be obtained. The value of $\beta_2 K_{\text{III}}$ is rather uncertain, because the second complex is present in very small amounts in the oxalate concentration range investigated. The solubility product, K_{III} , could consequently not be determined directly. The "best" value of the solubility product is probably obtained by dividing $K_{\text{III}}\beta_{3(\text{sol})}$ by $\beta_{3(\text{extr})}$. The corresponding solubility products for the solids Sc_2A_3 and NaScA_2 (K_{I} and K_{II}) were calculated by using eqns. (5) and (6). The results are given in Table 5.

POTENTIOMETRIC MEASUREMENTS

At high ligand concentrations it was possible to obtain supersaturated solutions with scandium concentrations sufficiently large for potentiometric measurements. The method used was the standard method of obtaining corresponding values of $\bar{n}$ and $[A]$ by emf-measurements of h .

Table 5. Results from the extraction and solubility studies and the final stability constants and solubility products. The errors are given as three standard deviations.
 $K^* = K_{\text{III}}^{-1} \times 10^{-18}$ (K_{I} , K_{II} , and K_{III} are defined on p. 163).

Constant	Extraction measurements	Solubility measurements	Final set
$\beta_1 \times 10^{-7} \text{ M}$	1.37 ± 0.07	—	1.37 ± 0.07
$\beta_2 \times 10^{-13} \text{ M}^2$	4.9 ± 0.3	$(3.2 \pm 2.4) \times K^*$	4.9 ± 0.3
$\beta_3 \times 10^{-15} \text{ M}^3$	4.8 ± 0.5	$(3.7 \pm 0.3) \times K^*$	4.8 ± 0.5
$\beta_4 \times 10^{-17} \text{ M}^4$	1.3 ± 0.3	$(1.55 \pm 0.08) \times K^*$	2.0 ± 0.5
$K_3 \times 10^{-9} \text{ M}$	9.8 ± 1.4	11.6 ± 9.6	—
$K_4 \text{ M}$	28 ± 8	42 ± 6	—
$K_{\text{III}} \times 10^{20} \text{ M}^{-7}$	—	—	7.7 ± 1.4
$K_{\text{I}} \text{ M}^{-4}$	—	—	$\sim 1 \times 10^{-27}$
$K_{\text{II}} \text{ M}^{-4}$	—	—	$\sim 1 \times 10^{-16}$

Experimental

The type of cells used and the experimental technique have been described previously.¹ (Glass electrode was used.) The ionic strength was 1.00 M and the temperature $20.0 \pm 0.1^\circ\text{C}$. Titrations were made at three different scandium concentrations, viz. 2.4 mM, 5.0 mM, and 10.0 mM, while the total ligand concentration varied between 28 mM and 76 mM. The value of h was in the range 10^{-3} to 10^{-4} M. All the titrations were started at high ligand concentration which was decreased until a solid phase was formed. The reproducibility was sometimes rather poor. Emf-values which could not be reproduced within 0.5 mV were not used to determine $\bar{n}$.

Results

Satisfactory potentiometric measurements have been made over a fairly narrow range of free oxalate concentration. The results have not been used to compute stability constants. However, a comparison has been made between the potentiometric $\bar{n}$ -values and those calculated from the final stability constants obtained from the two other methods. In the concentration range $10^{-3} \text{ M} < [\text{A}] < 10^{-2} \text{ M}$ the differences between these $\bar{n}$ -values are usually within 0.02 units. In solutions where the free oxalate concentration exceeds 10^{-2} M , the value of $\bar{n}_{\text{final}} - \bar{n}_{\text{pot}}$ is positive and rapidly increasing with increasing oxalate concentration. In some cases, especially when h is very low at the beginning of the series, the calculated $\bar{n}_{\text{pot}}$ -curve passes through a maximum. This seems to indicate some experimental errors or some wrong assumptions; e.g. some hydrolysed species may be formed.

Some $\bar{n}$ -values from the potentiometric measurements are shown in Fig. 1 together with the final $\bar{n}$ -curve. Six titration series are here represented in the range $h > 10^{-4} \text{ M}$. (Data are thus omitted in the beginning of some series.)

DISCUSSION

The final set of stability constants is chosen from the extraction and solubility measurements. The values $\beta_1 - \beta_3$ are directly taken from the extraction study. The value of $K_4 = \beta_4 \beta_3^{-1}$ determined with this method seems to be more

uncertain than the value obtained in the solubility investigation. The final value of β_4 is thus calculated from $K_{4(\text{sol})} \cdot \beta_{3(\text{extr})}$. The "best" stability constants with their estimated maximum errors are given in Table 5. The full-drawn curves in Figs. 1 and 2 are calculated by using this set of constants. From the figures it is obvious that a good description of the experimental findings is obtained.

The existence of polynuclear species has been examined by varying the total scandium concentration in the extraction measurements. No differences outside the expected experimental errors could be detected. At high oxalate concentrations ($[A] > 10^{-3}$ M) data are available from all the methods. The scandium concentration is here varied from about 10^{-6} M (extraction) to 10^{-3} M (solubility) and 10^{-2} M (potentiometry). The fact that these measurements can be described with the same set of stability constants is a good indication that no polynuclear species are formed in this oxalate concentration range.

In the range 10^{-6} M $< [A] < 10^{-4}$ M the distribution ratios were determined at varying values of $[A]$ and h . Similar variations were also made in the other two methods in the range $[A] > 10^{-3}$ M. As the various properties X , S , or $\bar{n}$ did not vary with h for a given value of $[A]$, one could conclude that no acid or hydroxo complexes were formed. (Some deviations in the potentiometric study have been discussed above.) The good description of the experimental material with species of the type ScA_3^{3-2f} only, is of course also a good indication that no mixed complexes are formed in larger amounts in the concentration ranges used. The existence of a complex ScHA^{2+} could hardly be established even in the most acid solutions if the constant $[\text{ScHA}] \cdot [\text{Sc}]^{-1} \cdot [\text{HA}]^{-1}$ is smaller than about 10^3 M. The value of this constant is probably about the same as the β_1 -value of the scandium acetate system. The latter constant is equal to $1.4 \times 10^3 \text{ M}^{-1}$ in a medium with ionic strength 0.1 M (NaClO_4) and at 25°C .¹⁷

The over-all stability constants for the scandium oxalato complexes are larger than the corresponding constants for the lanthanoid complexes.² This might be caused by the smaller ionic radius of scandium. The stepwise stability constants also show that the two last complexes are relatively weak compared to the two first ones. The K_1 -value of scandium is about 70 times larger than the corresponding value of lutetium. The K_2 -value is about 20 times larger. The values of K_3 and K_4 for scandium are on the other hand smaller than the corresponding Lu-values (1/2 and 1/3, respectively). The relative weakness of the two highest complexes is also seen from the presence of a weak plateau around $\bar{n}$ equal to 2 in the curve of Fig. 1. Similar trends, sometimes said to be caused by "steric hindrance", have been discussed previously for other ligands (cf. Ref. 1, p. 626).

Acknowledgements. I am indebted to my teacher, Dr. Ingmar Grenthe, who has given me all possible help and encouragement. This investigation has in part been supported by a grant from *Statens Naturvetenskapliga Forskningsråd* (Swedish Natural Science Research Council).

REFERENCES

1. Grenthe, I. and Hansson, E. *Acta Chem. Scand.* **23** (1969) 611.
 2. Grenthe, I., Gårdhammar, G. and Rundcrantz, E. *Acta Chem. Scand.* **23** (1969) 93.
- Acta Chem. Scand.* **25** (1971) No. 1

3. Korenman, I. M. and Zaglyadimova, N. V. *Zh. Neorg. Khim.* **11** (1966) 2774.
4. Kumok, V. N., Skorik, N. A. and Serebrennikov, V. V. *Tr. Tomsk. Gos. Univ. Ser. Khim.* **185** (1965) 129.
5. Starý, J. *Anal. Chim. Acta* **28** (1963) 132.
6. Gridasova, R. K., Kolosov, I. V. and Ivanov-Emin, B. N. *Radiokhimiya* **10** (1968) 37.
7. Grenthe, I. and Tobiasson, I. *Acta Chem. Scand.* **17** (1963) 2101.
8. Taft, R. W., Jr. and Cook, E. H. *J. Am. Chem. Soc.* **81** (1959) 46.
9. Reid, J. C. and Calvin, M. *J. Am. Chem. Soc.* **72** (1950) 2948.
10. King, E. L. and Reas, W. H. *J. Am. Chem. Soc.* **73** (1951) 1804.
11. Norén, B. *Acta Chem. Scand.* **21** (1967) 2435.
12. Bidermann, G., Kilpatrick, M., Pokras, L. and Sillén, L.-G. *Acta Chem. Scand.* **10** (1956) 1327.
13. Aveston, J. *J. Chem. Soc.* **1966** 1599.
14. Grenthe, I. and Williams, D. R. *Acta Chem. Scand.* **21** (1967) 341.
15. Rossotti, F. J. C. and Rossotti, H. *The Determination of Stability Constants*, McGraw, New York, Toronto, London 1961.
16. Gmelin-Kraut, *Handbuch der anorganischen Chemie*, Heidelberg 1932, Band VI, Abteilung 2, p. 688.
17. Kaleeva, V. A., Kumok, V. N. and Serebrennikov, V. V. *Tr. Tomsk. Gos. Univ. Ser. Khim.* **185** (1965) 141.

Received May 29, 1970.

Ref. C

Thermodynamic Properties of Rare Earth Complexes

X. Complex Formation in Aqueous Solution of Eu(III) and Iminodiacetic Acid

INGMAR GRENTHE and GÖRAN GÄRDHAMMAR

*Division of Physical Chemistry 1, Chemical Center, University of Lund,
P.O.B. 740, S-220 07 Lund 7, Sweden*

The stability constants for the formation of the complexes EuA_r^{3-2r} ($r=1-3$), EuHA^{2+} , and $\text{EuH}_2\text{A}^{3+}$ (H_2A denotes iminodiacetic acid) have been determined at 25.0°C in an aqueous sodium perchlorate medium with ionic strength 1.00 M. A potentiometric standard method was used, *viz.* emf-measurements of the hydrogen ion concentration.

Lanthanoid (III) iminodiacetate complexes in aqueous solution have been described earlier.¹⁻⁴ The investigators have usually interpreted their experimental data by assuming that the complexes MA^+ and MA_2^- are formed (M is one of the lanthanoids). In one study,² the possible existence of the complex MA_3^{3-} is mentioned. It is difficult to estimate how well the previous authors can describe their experimental findings, as no primary data are given in the publications.

The existence of complexes $\text{M}_p\text{H}_q\text{A}_r^{3p+q-2r}$ with $q > 0$ can be regarded as rather probable, because of the strong basicity of the ion A^{2-} . H_2A exists in water mainly in the dipolar form $\text{HOOC}\cdot\text{CH}_2\cdot\text{NH}_2^+\cdot\text{CH}_2\cdot\text{COO}^-$ (*cf.* Ref. 5), and both H_2A and HA^- consequently should be able to coordinate to the central ion. Complexes with both HA^- and A^{2-} as ligands have been found in the solid state, *e.g.* $\text{M}_2(\text{HA})_2\text{A}(\text{ClO}_4)_2\cdot 7\text{H}_2\text{O}$ and $[\text{MA}(\text{H}_2\text{O})_3]\text{Cl}$.^{6,7}

The present study of the europium(III) iminodiacetate system was performed to find out if metal complexes other than EuA^+ and EuA_2^- might be formed, and to make a comparison with other dicarboxylate ligands (*vide* Part IX in this series⁸).

The experimental method used in this investigation is the same as in the earlier studies,¹⁻⁴ *i.e.* a potentiometric determination of the hydrogen ion concentration by means of a glass electrode. All measurements were performed in a medium with ionic strength 1.00 M, using sodium perchlorate as the neutral salt. The temperature was $(25.0 \pm 0.1)^\circ\text{C}$.

The symbols used in the following have been defined previously.⁸

EXPERIMENTAL

Chemicals. Stock solutions of europium(III) perchlorate and sodium perchlorate were prepared and analysed as described previously.⁸ Iminodiacetic acid (The British Drug Houses Ltd.) was used without further purification. The purity was checked by potentiometric titrations with sodium hydroxide. The experimental formula weight was 133.2. The theoretical value is 133.1.

Potentiometric determination of stability constants. The galvanic cells used and the titration technique have been described earlier.⁸ The various S- and T-solutions, whose compositions are given in Table 1, were prepared from stock solutions of europium perchlorate, iminodiacetic acid, sodium perchlorate and perchloric acid or sodium hydroxide.

Table 1. Composition of the various S- and T-solutions. The related values of V_0 and the ranges of $\bar{n}_H$ are also given. (Series 1–9 refer to the proton system, series 10–23 to the Eu system.)

Ser.	C_{HS} mM	C_{MS} mM	C_{AS} mM	C_{HT} mM	C_{MT} mM	C_{AT} mM	V_0 ml	Range ^a
1	20.30	0	10.15	— 24.50	0	0	20.00	1.70–1.11
2	20.30	0	10.15	— 24.50	0	0	15.00	1.70–1.14
3	20.30	0	10.15	— 24.50	0	0	15.00	1.70–1.08
4	20.30	0	10.15	53.9	0	0	15.00	1.70–2.40
5	239.6	0	119.8	590	0	0	15.00	1.96–2.42
6	71.0	0	35.50	173.7	0	0	20.00	1.87–2.45
7	239.6	0	119.8	— 198.1	0	0	15.00	1.96–0.35
8	71.0	0	35.50	— 198.1	0	0	25.00	1.87–0.44
9	239.6	0	119.8	— 996	0	0	25.00	1.96–0.38
10	25.00	14.18	25.00	143.1	14.18	25.00	15.00	0.99–2.31
11	25.00	44.7	25.00	139.5	44.7	25.00	15.00	0.99–2.21
12	15.72	29.82	15.72	145.3	29.82	15.72	20.00	0.98–2.31
13	25.00	29.82	25.00	139.0	29.82	25.00	15.00	0.99–2.27
14	14.19	7.09	25.00	145.7	7.09	25.00	20.00	0.64–1.27
15	29.16	29.82	50.0	107.8	29.82	50.0	20.00	0.58–1.25
16	28.63	14.91	50.0	107.2	14.91	50.0	15.00	0.57–1.23
17	32.06	7.09	40.0	273.3	7.09	40.0	20.00	0.80–1.32
18	23.29	20.87	50.0	107.4	20.87	50.0	15.00	0.47–1.25
19	52.8	7.09	50.0	— 98.5	0	0	20.00	1.05–0.43
20	164.5	41.3	156.3	— 198.1	0	0	20.00	1.05–0.18
21	103.1	7.09	100.0	— 98.5	0	0	15.00	1.03–0.60
22	101.9	29.82	100.0	— 98.5	0	0	15.00	1.02–0.08
23	26.41	3.54	25.00	— 98.5	0	0	25.00	1.05–0.39

The glass electrodes used in acid and alkaline solutions were of type Beckman 40498 and Beckman 40495, respectively. Ag, AgCl electrodes were prepared according to Brown.⁹

Contamination of the solutions with carbon dioxide was prevented by passing a stream of nitrogen through the solution in the titration vessel.

The measured emf-values were corrected for the liquid junction potential as described before.⁸

All titrations were repeated at least twice. The reproducibility of the emf was usually within 0.1 mV. In the most alkaline solutions the emf-values sometimes could be reproduced only within (0.3–0.4) mV.

CALCULATION AND RESULTS

The proton iminodiacetate system. The protonation constants β_{0q1} ($q=1-3$) were determined by the graphical standard methods of Leden and Fronæus.¹⁰ The values were then refined by the least squares program LETAGROP VRID.¹¹ The titration series used in the final calculation are given in Tables 1 and 2 (series 1-9). The following results were obtained:

$$\begin{aligned}\beta_{011} &= (2.064 \pm 0.035) \times 10^9 \text{ M}^{-1} \\ \beta_{021} &= (7.77 \pm 0.17) \times 10^{11} \text{ M}^{-2} \\ \beta_{031} &= (5.91 \pm 0.13) \times 10^{13} \text{ M}^{-3}\end{aligned}$$

The standard deviation in the error-carrying variable C_H/C_A (denoted *sig y* in the following) is equal to 6.28×10^{-3} . The errors in the above and the following constants are always given as three standard deviations.

The europium iminodiacetate system. The method of calculating stability constants was the same as described before.⁸ The titration series used are given in Tables 1 and 2 (series 10-23). The experimental data could be described rather well by assuming the formation of the metal complexes EuA_r^{3-2r} ($r=1-3$), EuHA^{2+} and $\text{EuH}_2\text{A}^{3+}$. The following final constants were obtained in the least squares refinement (*sig y* = 5.28×10^{-3}):

$$\begin{aligned}\beta_{101} &= (3.08 \pm 0.10) \times 10^6 \text{ M}^{-1} \\ \beta_{102} &= (4.43 \pm 0.19) \times 10^{11} \text{ M}^{-2} \\ \beta_{103} &= (5.01 \pm 0.29) \times 10^{15} \text{ M}^{-3} \\ \beta_{111} &= (6.23 \pm 0.21) \times 10^{10} \text{ M}^{-2} \\ \beta_{121} &= (7.26 \pm 0.80) \times 10^{12} \text{ M}^{-3}\end{aligned}$$

Some other combinations of metal complexes were also tried with the LETAGROP VRID program. A trial of EuHA_2 lies near at hand. Complexes of corresponding composition have been found in the malonate⁸ and thiodiacetate¹² systems. A refinement with this complex included gave a value of $\beta_{112} = (1 \pm 1) \times 10^{16} \text{ M}^{-3}$, while the value of *sig y* remained practically unchanged. Hence, the complex EuHA_2 is present in very small amounts, if at all, in the solutions studied. A trial of the complex EuH_2A_2^+ and some binuclear species gave similar results.

Finally, a calculation of the protonation constants was made in solutions where $C_M \neq 0$. The final europium constants, β_{1qr} , were kept constant, while the protonation constants, β_{0q1} , were varied. The new β_{0q1} -values differ very little (0.5-0.6 %) from those obtained when $C_M = 0$.

Fig. 1 shows the distribution of the various europium complexes as a function of $\log(a/M)$ at three different values of h , viz. 10^{-2} M , 10^{-4} M and 10^{-6} M . The values of a at these hydrogen ion concentrations cannot exceed $6 \times 10^{-9} C_A$, $5 \times 10^{-8} C_A$, and $5 \times 10^{-4} C_A$, respectively.

The differences $(C_{H(\text{calc})}/C_A) - (C_{H(\text{exp})}/C_A)$ are also given in Table 2. From these values it is obvious that systematic errors are present in some of the titration series. The errors are very small and may be caused for instance by small analytical errors in the S- and T-solutions.

$$(C_{H(\text{calc})} - C_{H(\text{exp})}) C_A^{-1} \times 10^3.$$

v/ml	-lg(h/v)	Δv	v/ml	-lg(h/v)	Δv	v/ml	-lg(h/v)	Δv	v/ml	-lg(h/v)	Δv	v/ml	-lg(h/v)	Δv	v/ml	-lg(h/v)	Δv
Series 1			Series 2			Series 10			Series 16			Series 19			Series 22		
0.00	2.512	2.87	0.00	2.343	3.58	0.00	3.640	-6.95	0.00	5.629	2.93	0.00	3.694	-1.18	0.00	3.687	1.98
1.00	2.551	5.90	0.50	2.429	2.93	0.10	3.521	-7.45	0.20	5.541	3.26	0.20	3.920	-0.91	0.50	3.668	1.18
1.50	2.595	3.14	1.00	2.520	3.01	0.20	3.408	-6.75	0.40	5.459	3.44	0.40	4.145	-0.64	1.00	4.037	2.24
2.00	2.644	3.90	1.50	2.572	3.07	0.30	3.377	-6.40	0.60	5.377	3.44	1.00	4.303	-0.16	1.50	4.208	2.64
2.50	2.683	3.90	2.00	2.733	-0.53	0.40	3.219	-6.40	0.80	5.301	3.14	1.20	4.490	0.12	2.40	4.370	2.04
3.00	2.744	4.57	2.50	2.862	-1.29	0.50	3.139	-5.74	1.10	5.190	3.08	1.40	4.635	0.50	3.00	4.527	2.75
3.50	2.843	-0.09	3.00	3.019	-2.49	0.65	3.038	-5.59	1.40	5.085	2.90	1.60	4.781	0.82	3.50	4.679	2.77
4.00	2.904	2.49	3.30	3.125	-3.52	0.80	2.965	-5.56	1.70	4.985	2.69	1.80	4.926	0.96	4.20	4.833	0.00
4.50	2.968	0.59	3.60	3.235	-3.66	1.00	2.855	-6.64	2.00	4.885	2.49	2.00	5.071	1.33	4.80	4.987	-0.97
5.00	3.041	0.87	3.80	3.272	-3.44	1.20	2.771	-5.38	2.30	4.796	2.27	2.30	5.293	1.91	5.40	5.148	-2.25
5.50	3.127	0.80	4.00	3.372	-3.18	1.40	2.700	-6.28	2.60	4.716	1.84	2.60	5.493	2.07	6.00	5.311	-0.77
6.00	3.224	-0.65	4.10	3.416	-1.70	1.60	2.634	-5.09	2.90	4.618	1.47	2.70	5.597	2.22	6.60	5.482	-5.55
6.50	3.344	-1.31	4.30	3.532	1.39	1.80	2.524	-5.39	3.20	4.530	1.39	2.90	5.751	2.78	7.20	5.658	-5.66
7.00	3.496	-0.47	4.50	3.627	-1.40	2.00	2.433	-7.28	3.50	4.444	1.06	3.10	5.910	3.22	7.80	5.839	-5.67
			5.10	3.817	1.05	2.20	2.356	-10.87	3.80	4.358	0.75	3.30	6.073	3.69	8.40	6.022	-5.66
			5.30	3.860	1.61	2.30	2.335	-10.75	4.10	4.272	0.41	3.50	6.233	5.09	9.00	6.187	-7.99
			5.50	3.779	2.24	2.40	2.150	-9.81	4.40	4.186	0.02	3.70	6.402	5.82	9.60	6.351	-5.77
			5.70	3.082	2.76	2.50	2.076	-7.85	4.70	4.098	0.01	3.90	6.571	6.99	10.20	6.486	-5.01
			5.90	3.975	3.24	2.60	1.993	-12.62	5.00	4.015	-0.53	4.10	6.753	7.91	10.80	6.622	-1.56
			6.25	3.123	3.40	2.70	1.910	-6.51	5.30	3.932	-0.82	4.30	6.948	7.45	11.40	6.764	-6.02
			6.60	3.260	4.41	2.80	1.831	-16.20	5.60	3.797	-1.13	4.50	7.111	6.76	12.00	6.907	0.95
			7.00	3.414	5.43	2.90	1.750	-10.81	6.20	3.699	-0.97	4.60	7.365	5.81	12.60	7.063	1.45
						3.00	1.670	-6.51	6.60	3.613	-1.18	4.70	7.512	4.98	13.20	7.228	1.99
						3.10	1.593	-1.01	7.00	3.535	-1.01	4.85	7.666	4.11	13.80	7.409	-2.82
						3.20	1.515	-2.97	7.50	3.450	-0.97	5.05	7.824	3.15	14.20	7.561	2.76
						3.30	1.437	-3.57	8.10	3.366	-0.97	5.05	7.967	2.42	14.80	7.732	-2.46
						3.40	1.360	-4.18	8.90	3.271	-0.51	5.20	8.092	1.91	15.40	7.908	-1.68
						3.50	1.283	-4.79	9.90	3.176	-0.50	5.30	8.250	1.20	16.00	8.083	1.50
						3.60	1.206	-5.40	11.30	3.073	0.70	5.40	8.410	0.10	17.00	8.165	-0.40
						3.70	1.129	-6.01				5.50	8.542	0.31	18.00	8.346	-0.34
						3.80	1.052	-6.62				5.60	8.674	0.52	19.00	8.527	-0.38
						3.90	0.975	-7.23				5.70	8.806	-0.80	20.00	8.708	-1.37
						4.00	0.898	-7.84				5.80	8.938	-1.01	21.00	8.889	-1.37
						4.10	0.821	-8.45				5.90	9.070	-1.22	22.00	9.070	9.08
						4.20	0.744	-9.06				6.00	9.202	-1.43	23.00	9.251	9.26
						4.30	0.667	-9.67				6.10	9.334	-1.64	24.00	9.432	9.45
						4.40	0.590	-10.28				6.20	9.466	-1.85	25.00	9.613	9.64
						4.50	0.513	-10.89				6.30	9.598	-2.06	26.00	9.794	9.87
						4.60	0.436	-11.50				6.40	9.730	-2.27	27.00	9.975	10.10
						4.70	0.359	-12.11				6.50	9.862	-2.48	28.00	10.156	10.33
						4.80	0.282	-12.72				6.60	9.994	-2.69	29.00	10.337	10.56
						4.90	0.205	-13.33				6.70	10.126	-2.90	30.00	10.518	10.79
						5.00	0.128	-13.94				6.80	10.258	-3.11	31.00	10.699	11.02
						5.10	0.051	-14.55				6.90	10.390	-3.32	32.00	10.880	11.25
						5.20	-0.026	-15.16				7.00	10.522	-3.53	33.00	11.061	11.48
						5.30	-0.103	-15.77				7.10	10.654	-3.74	34.00	11.242	11.71
						5.40	-0.180	-16.38				7.20	10.786	-3.95	35.00	11.423	11.94
						5.50	-0.257	-16.99				7.30	10.918	-4.16	36.00	11.604	12.17
						5.60	-0.334	-17.60				7.40	11.050	-4.37	37.00	11.785	12.40
						5.70	-0.411	-18.21				7.50	11.182	-4.58	38.00	11.966	12.63
						5.80	-0.488	-18.82				7.60	11.314	-4.79	39.00	12.147	12.86
						5.90	-0.565	-19.43				7.70	11.446	-5.00	40.00	12.328	13.09
						6.00	-0.642	-20.04				7.80	11.578	-5.21	41.00	12.509	13.32
						6.10	-0.719	-20.65				7.90	11.710	-5.42	42.00	12.690	13.55
						6.20	-0.796	-21.26				8.00	11.842	-5.63	43.00	12.871	13.78
						6.30	-0.873	-21.87				8.10	11.974	-5.84	44.00	13.052	14.01
						6.40	-0.950	-22.48				8.20	12.106	-6.05	45.00	13.233	14.24
						6.50	-1.027	-23.09				8.30	12.238	-6.26	46.00	13.414	14.47
						6.60	-1.104	-23.70				8.40	12.370	-6.47	47.00	13.595	14.70
						6.70	-1.181	-24.31				8.50	12.502	-6.68	48.00	13.776	14.93
						6.80	-1.258	-24.92				8.60	12.634	-6.89	49.00	13.957	15.16
						6.90	-1.335	-25.53				8.70	12.766	-7.10	50.00	14.138	15.39
						7.00	-1.412	-26.14				8.80	12.898	-7.31			
						7.10	-1.489	-26.75				8.90	13.030	-7.52			
						7.20	-1.566	-27.36				9.00	13.162	-7.73			
						7.30	-1.643	-27.97				9.10	13.294	-7.94			
						7.40	-1.720	-28.58				9.20	13.426	-8.15			
						7.50	-1.797	-29.19				9.30	13.558	-8.36			
						7.60	-1.874	-29.80				9.40	13.690	-8.57			
						7.70	-1.951	-30.41				9.50	13.822	-8.78			
						7.80	-2.028	-31.02				9.60	13.954	-8.99			
						7.90	-2.105	-31.63				9.70	14.086	-9.20			
						8.00	-2.182	-32.24				9.80	14.218	-9.41			
						8.10	-2.259	-32.85				9.90	14.350	-9.62			
						8.20	-2.336	-33.46				10.00	14.482	-9.83			
						8.30	-2.413	-34.07				10.10	14.614	-10.04			
						8.40	-2.490	-34.68				10.20	14.746	-10.25			
						8.50	-2.567	-35.29				10.30	14.878	-10.46			
						8.60	-2.644	-35.90				10.40	15.010	-10.67			
						8.70	-2.721	-36.51				10.50	15.142	-10.88			
						8.80	-2.798	-37.12				10.60	15.274	-11.09			
						8.90	-2.875	-37.73				10.70	15.406	-11.30			
						9.00	-2.952	-38.34				10.80	15.538	-11.51			
						9.10	-3.029	-38.95				10.90	15.670	-11.72			
						9.20	-3.106	-39.56				11.00	15.802	-11.93			
						9.30	-3.183	-40.17				11.10	15.934	-12.14			
						9.40	-3.260	-40.78				11.20	16.066	-12.35			
						9.50	-3.337	-41.39				11.30	16.198	-12.56			
						9.60	-3.414	-42.00				11.40	16.330	-12.77			
						9.70	-3.491	-42.61				11.50	16.462	-12.98			
						9.80	-3.568	-43.22				11.60	16.594	-13.19			
						9.90	-3.645	-43.83									

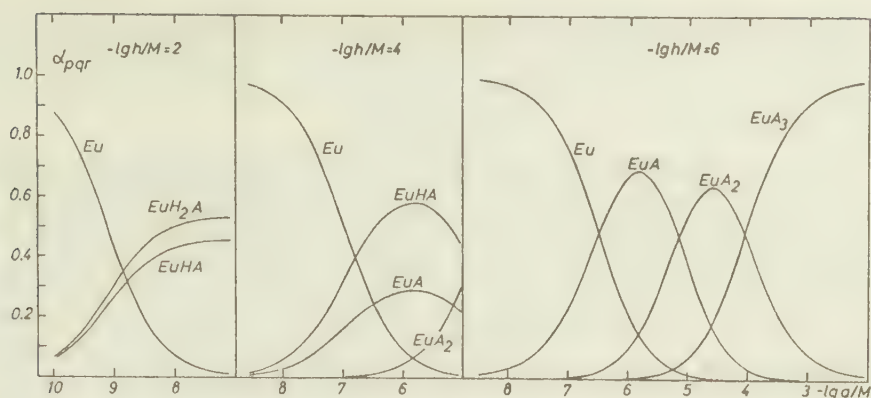


Fig. 1. Distribution curves at various hydrogen ion concentrations. α_{pqr} is plotted versus $-\log(a/M)$.

DISCUSSION

Several investigations of the proton iminodiacetate system have been carried out previously.^{2-4,13} Table 3 shows the constants obtained. The values of β_{011} and β_{021} found in the present study agree well with the previous results obtained under similar experimental conditions. The species H_3A^+ has not been detected in any of these studies. Its existence has been indicated, however, in an IR investigation⁵ of a solution where $\log(h/M) = -0.4$. Our study has shown that H_3A^+ is present in fairly large amounts also in solutions of pure iminodiacetic acid. $[H_3A^+]/C_A$ has (in 1 M $NaClO_4$) values between 0.11 and 0.22, if C_A is in the range 0.01 M to 0.12 M.

A comparison of the values of β_{101} and β_{102} for the europium iminodiacetate systems investigated is given in Table 3 (Ref. 1-3, and this study). The

Table 3. Stability constants β_{pqr} obtained in different studies. All investigations were performed at 25°C. (I =ionic strength.)

I/M and inert salt	$\log(\beta_{011}M)$	$\log(\beta_{021}M^2)$	$\log(\beta_{101}M)$	$\log(\beta_{102}M^2)$	Ref.
0.1 (KCl)	—	—	7.26	—	1
0.1 (KNO ₃)	9.33	11.91	6.73	12.11	2
0.3 (KCl)	9.60	12.61	6.22	10.94	3
0.1 (KNO ₃)	9.34	11.94	—	—	4
0.1 (KNO ₃)	9.40	11.90	—	—	13
1 (KNO ₃)	9.38	11.93	—	—	13
1 (NaClO ₄)	9.32	11.89	6.49	11.65	This study

differences can be explained by the fact that previous investigators have not taken into account the species H_3A^+ , MHA^{2+} , MH_2A^{3+} , and MA_3^{3-} (in one study,¹ only MA^+ was considered).

The possible existence of the complex MA_3^{3-} is mentioned by Thompson.² Prutkova and Martynenko⁴ have investigated the Nd and Yb iminodiacetate systems. Some of their $\bar{n}$ -curves show that a third complex is formed. Nevertheless, these authors used only two constants to describe their experimental data.

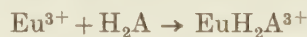
If too few titrations are made, it may sometimes be difficult to discover mixed complexes. In some cases, not even a relatively large variation of the ratio $C_{\text{H}}/C_{\text{A}}$ does reveal the formation of such species. This point was discussed in some detail in the preceding communication.⁸ It is possible to get a fairly good description of most of the experimental material, using only the species EuA_r^{3-2r} . From the titration series 14–18, the following values were obtained: $\beta_{101} = (1.37 \pm 0.12) \times 10^6 \text{ M}^{-1}$, $\beta_{102} = (2.1 \pm 0.3) \times 10^{11} \text{ M}^{-2}$, $\beta_{103} = 5.0 \times 10^{15} \text{ M}^{-3}$ (not varied). The value of $\text{sig } y = 14.8 \times 10^{-3}$ is considerably higher than in the final calculation with the mixed complexes included. The errors $(C_{\text{H}(\text{calc})}/C_{\text{A}}) - (C_{\text{H}(\text{exp})}/C_{\text{A}})$ also tend to increase with increasing h . Hence, it is necessary to introduce the acid complexes in order to describe satisfactorily the entire experimental material.

The complexes EuA_r^{3-2r} are very stable, and at most three iminodiacetate ligands are coordinated. The shape of the $\bar{n}$ -curves at the highest values obtained ($2.9 < \bar{n} < 3.0$) clearly shows that a fourth complex, if formed at all, must be very weak. From the above findings it seems reasonable to assume that iminodiacetate acts as a three-dentate ligand, and that europium is at least nine-coordinated in the complex EuA_3^{3-} .

The ligand HA^- ($^-\text{OOC}\cdot\text{CH}_2\cdot\text{NH}_2^+\cdot\text{CH}_2\cdot\text{COO}^-$) is a potential chelating agent. The magnitude of the equilibrium constant, K_{EuHA} , for the reaction



should give an indication whether a chelate is formed or not. K_{EuHA} is equal to 30 M^{-1} and has the same magnitude as the corresponding constants in the malonate⁸ and thiodiacetate¹² systems. The value does not differ much from the β_1 -value in the europium acetate system,¹⁴ *i.e.* HA^- seems to be coordinated as a unidentate ligand. A similar coordination can also be expected for the dipolar ligand H_2A , since the equilibrium constant for the reaction



is as low as 9 M^{-1} . The difference in the relative stability between Eu^{3+} and the ligands HA^- and H_2A is negligible if the statistical factors for the two ligands are taken into account.

The coordinated ligands HA^- and H_2A are stronger acids than the corresponding free species. The increase in acid strength is much larger for EuHA^{2+} compared to HA^- than for $\text{EuH}_2\text{A}^{3+}$ compared to H_2A (a factor 10^5 as compared to 3). This large difference may be correlated with the large difference in distance between the dissociating proton and the coordinated metal ion in the two species.¹⁵

Note added in proof. Kupriyanova and Martynenko have in a recent communication (*Russ. J. Inorg. Chem.* **15** (1970) 1024) determined the stability constant for the tris-iminodiacetato complex of neodymium by a spectrophotometric method.

Acknowledgement. This investigation has in part been supported by a grant from the Swedish Natural Science Research Council.

REFERENCES

1. Harder, R. and Chaberek, S. J. *Inorg. Nucl. Chem.* **11** (1959) 197.
2. Thompson, L. C. *Inorg. Chem.* **1** (1962) 490.
3. Misumi, S. and Aihara, M. *Bull. Chem. Soc. Japan* **39** (1966) 2677.
4. Prutkova, N. M. and Martynenko, L. I. *Russ. J. Inorg. Chem.* **14** (1969) 801.
5. Nakamoto, K., Morimoto, Y. and Martell, A. E. *J. Am. Chem. Soc.* **84** (1962) 2081.
6. Albertsson, J. and Oskarsson, Å. *Acta Chem. Scand.* **22** (1968) 1700.
7. Oskarsson, Å. *Acta Chem. Scand.* **25** (1971) 1206.
8. Dellien, I. and Grenthe, I. *Acta Chem. Scand.* **25** (1971) 1387.
9. Brown, A. S. *J. Am. Chem. Soc.* **56** (1934) 646.
10. Rossotti, F. J. C. and Rossotti, H. *The Determination of Stability Constants*, McGraw, New York, Toronto, London 1961.
11. Ingri, N. and Sillén, L.-G. *Arkiv Kemi* **23** (1965) 97.
12. Dellien, I. and Grenthe, I. *To be published*.
13. Rajan, K. S. and Martell, A. E. *J. Inorg. Nucl. Chem.* **26** (1964) 789.
14. Grenthe, L. *Acta Chem. Scand.* **16** (1962) 1695.
15. Schwarzenbach, G. *Z. Physik. Chem. (Leipzig)* **A 176** (1936) 133.

Received August 21, 1970.

Ref. D

Thermodynamic Properties of Rare Earth Complexes

XIII. Free Energy, Enthalpy and Entropy Changes for the Formation of Rare Earth(III)-Iminodiacetate Complexes

Ingmar Grenthe and Göran Gårdhammar

Division of Physical Chemistry 1, Chemical Center,
University of Lund, P.O.B. 740, S - 220 07 Lund 7,
Sweden.

The changes in free energy, enthalpy and entropy for the formation of the complexes $MA_{\underline{r}}^{3-2\underline{r}}$ ($\underline{r} = 1 - 3$), MHA^{2+} and MH_2A^{3+} have been determined. M denotes a lanthanoid (Pr, Eu, Ho or Lu) and H_2A iminodiacetic acid. Stability constants for the complexes ScA^+ , ScA_2^- , $ScHA^{2+}$ and ScH_2A^{3+} have also been determined. All measurements have been performed at 25 °C in a medium with ionic strength 1.0 M using sodium perchlorate as the neutral salt.

The stoichiometric composition and the stability constants for the various complexes formed in the europium(III)-iminodiacetate system were described in a previous communication (part X in this series ¹). This investigation has been extended to include both free energy, enthalpy and entropy data for the formation of the corresponding praseodymium, europium, holmium and lutetium complexes. Free energy data have also been determined for some scandium iminodiacetate complexes. This choice of central ions has been made in order to investigate how the maximum number of coordinated ligands and the various thermodynamic quantities for the complex formation reactions are influenced by the size of the central ion. It has also been of interest to investigate how the thermodynamic properties are affected by a change of the donor atoms in various dicarboxylates (see part IX in this series ²). Such a comparison between different ligands is facilitated if more than one central ion is investigated.

All measurements were performed at 25.0 °C in a medium with ionic strength 1.0 M using sodium perchlorate as the neutral salt. The stability constants were determined by a potentiometric standard method, viz. emf-measurements of the hydrogen ion concentration. The enthalpy changes were obtained by calorimetric titrations.

The symbols not defined below are given in Ref 2.

NOTATION

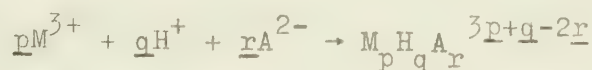
Q = the heat change after each addition of T-solution (cf. below).

Q_{corr} = the above heat change corrected for heats of dilution.

v = the total volume of added T-solution.

V_0 = the initial volume of S-solution (cf. below).

ΔG_{pqr}^0 , ΔH_{pqr}^0 , ΔS_{pqr}^0 = the over-all changes in free energy, enthalpy and entropy for the formation of one mole complex according to the reaction



CALCULATIONS

The calculation of the stability constants β_{pqr} has been described before ^{1,2}. It was assumed that the same species are predominant as those previously found in the europium system (for the scandium system, vide infra p. 5).

The enthalpy changes have been calculated by using the least-squares program "LETAGROP KALLE" ³. The entropy changes were calculated by use of the relation $\Delta S_{pqr}^0 = (\Delta H_{pqr}^0 - \Delta G_{pqr}^0)/T$

EXPERIMENTAL

Chemicals. The rare earth(III) perchlorates, iminodiacetic acid and sodium perchlorate were prepared and analyzed as described previously ^{1,4}.

Potentiometric measurements. The experimental technique was the same as described before ¹. Tables of the experimental emf data can be obtained from the authors.

Calorimetric measurements. The calorimeter used was of the type described in Ref 5. The precision and the accuracy of the calorimeter were tested by electrical calibrations and by a determination of the heat of neutralization of sodium hydroxide, respectively. Details of the procedures are given in Ref 5 and 6. The results agreed with those found previously ^{5,6}. (The experimental value for the heat

of neutralization corrected to infinite dilution was equal to -55.81 ± 0.06 kJ/mole).

The inner reaction vessel contained about 120 ml. It was initially filled with a solution S, whose volume (V_0) varied between 90.0 and 100.0 ml. Successive additions of 3.00 ml of a solution T were then made from a calibrated piston burette. The corresponding heat changes, Q , were obtained as described earlier^{5,6}. The heats of dilution of the various T-solutions were also determined while those of the S-solutions are known to be negligible⁷. The corrected heat changes, Q_{corr} , were then used in the least-squares computation. The analytical composition of the various S- and T-solutions are given in Table 1.

RESULTS

Determination of stability constants. The least-squares refined stability constants with their estimated errors, given as three standard deviations, are represented in Table 2. The standard deviation, sigy, in the error-carrying variable C_H/C_A (cf. Ref 1, p.1403) has also been included.

The values of the stability constants and particularly their standard deviations depend on the weighting scheme used in the least-squares refinement. All the experimental points have been assigned a weight of one in these calculations, and the experimental material has thus been weighted by the distribution of experimental points. In order to make comparisons between different lanthanoids it is advantageous to choose this distribution as similar as possible between the various systems. The stability constants of the europium system were recalculated by using only the titration series 10, 13, 14 and 19. These series have stoichiometric compositions, which are

rather similar to those used in the three other systems investigated. The recalculated values of the europium constants have been included in Table 2. They differ slightly from the values published previously (Ref 1, p. 1403).

The stability constants for the scandium system have been calculated from three titrations series. A satisfactory description of the experimental data could only be obtained in the range $1.8 < -\log(h/M) < 4.0$, presumably due to hydrolysis at lower hydrogen ion concentrations. The stability constants have a lower precision than those in the corresponding lanthanoid systems. This may be due to the presence of other species than those found in the lanthanoid systems, e.g. some hydroxo complexes. The fact that the data with high free ligand concentrations are rather uncertain makes it difficult to find out whether a complex ScA_3^{3-} is formed or not. The experimental material seems to indicate that such a complex ought to be very weak if formed at all. (The $\bar{n}$ versus $[A^{2-}]$ -curve shows a clear plateau at $\bar{n} = 2$ for $-5.0 < \log([A]/M) < -4.0$).

Determination of enthalpy changes. The experimental Q -values are positive for exothermal and negative for endothermal reactions.

The various heats of dilution are given in Table 3. The experimental data for the protonation and metal complexation reactions in the various iminodiacetate systems are collected in Table 4. Values of the quantity

$$\Delta Q = Q_{\text{corr, calc.}} - Q_{\text{corr, exp.}}$$

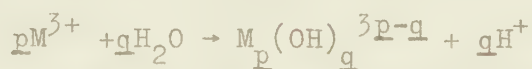
have also been included in this table in order to show how well the experimental data can be described by the various molar enthalpy changes. These are given in Table 5 with their errors, estimated as three standard deviations. The least-squares refinements of the calorimetric data have been made by using the stability constants β_{pqr} given in Table 2.

The hydrogen ion concentration is rather low in the latter part of some of the calorimetric titrations. Hence, the reaction



must be considered. In the final least-squares computations this reaction has been included by using values of K_w and enthalpy of neutralization equal to $1.70 \times 10^{-14} \text{ M}^2$ (c.f. Ref 8) and -56.11 kJ/mole (c.f. Ref 9) respectively. The corrections for the neutralization reaction are relatively small; at most corresponding to 0.13 J in an individual measurement and 0.16 kJ/mole in a computed enthalpy change.

An estimate of the possible influence of hydrolysis products on the enthalpy values has also been made. We have assumed that the only hydroxo complexes present are MOH^{2+} and $\text{M}_2(\text{OH})_2^{4+}$. The stability constants used were the same as those for the corresponding yttrium complexes ¹⁰. The enthalpy changes for the reactions

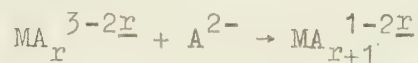


have been estimated as $50 - 50 \text{ kJ/mole}$ from the compilation made by Arnek ¹¹. A calculation of the influence of hydroxide complexation reactions to the measured Q -values showed that the contribution always was small, at most 0.01 J in an individual measurement. Hence, these hydroxo complexes have been neglected in the computations.

Some attempts were made to vary enthalpy values and stability constants simultaneously. The only quantities varied in these calculations were one of β_{pqr} and the corresponding $\Delta H^\circ_{\text{pqr}}$ -value. In all cases except for the complex MH_2A^{3+} the results confirm the magnitude of the potentiometrically determined stability constants. No calculation was possible for MH_2A^{3+} because of the low concentrations of this species.

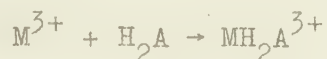
DISCUSSION

The variations in the thermodynamic functions $\underline{\Delta H}^0$ and $\underline{\Delta S}^0$ for the stepwise reactions



through the lanthanoid series seem to follow the patterns observed earlier for the diglycolate and dipicolinate systems ⁷.

The ion HA^- acts as ligand in a similar way as the bimalonate ion ² and the acetate ion ¹³⁻¹⁵. The $\underline{\Delta G}^0$ -values for the reaction



also vary in a manner similar to the acetate system.

The errors in the corresponding $\underline{\Delta H}^0$ and $\underline{\Delta S}^0$ -values are too large to warrant a comparison between the various lanthanoids.

The strength of the acid MHA^{2+} increases with increasing atomic number from 2.15×10^{-5} for Pr to 29.0×10^{-5} for Lu in much the same way as was found previously in the lanthanoid malonate system (Ref 2, p. 1399). The first dissociation constant of the acid MH_2A^{3+} remains on the other hand nearly constant throughout the lanthanoid series.

A comparison between the scandium system and the lanthanoid systems shows the same type of "steric hindrance" for the formation of a third complex for small central ions as was found previously in other dicarboxylate systems ^{4,16}. Already the second scandium complex is relatively weak compared to the first one.

Acknowledgement. We want to thank Professor Ido Leden for useful discussions and valuable comments and fil lic Lennart Kullberg for valuable advice. This investigation has partly been supported by a grant from the Swedish Natural Science Research Council.

REFERENCES

1. Grenthe, I. and Gårdhammar, G.
Acta Chem. Scand. 25 (1971) 1401.
2. Dellien, I. and Grenthe, I.
Acta Chem. Scand. 25 (1971) 1387.
3. Arnek, R.
Arkiv för kemi 32 (1970) 81.
4. Gårdhammar, G.
Acta Chem. Scand. 25 (1971) 158.
5. Grenthe, I., Ots, H. and Ginstруп, O.
Acta Chem. Scand. 24 (1970) 1067.
6. Åhrland, S. and Kullberg, L.
Acta Chem. Scand. 25 (1971)
7. Grenthe, I.
Acta Chem. Scand. 17 (1963) 2487.
8. Näsänen, R. and Meriläinen, P.
Suomen Kem. 33 B (1960) 149.
9. Vasil'ev, V.P. and Lobanov, G.A.
Izvest. V.U.Z. Khim. i Khim. Tekhnol. 12 (1969) 740.

10. Biedermann, G. and Ciavatta, L.

Arkiv för kemi 22 (1964) 253.

11. Arnek, R.

Arkiv för kemi 32 (1970) 55.

12. Dellien, I. and Grenthe, I.

To be published.

13. Sonesson, A.

Acta Chem. Scand. 12 (1958) 165.

14. Sonesson, A.

Acta Chem. Scand. 12 (1958) 1937.

15. Grénthe, I.

Acta Chem. Scand. 18 (1964) 283.

16. Grénthe, I. and Hansson, E.

Acta Chem. Scand. 23 (1969) 611.

Table 1. Composition of the various S- and T-solutions in the calorimetric titrations.

Series 1 - 4 represent the proton system. $\frac{C_M(T)}{C_M(T)} = 0$ in all cases.

Series	Metal	$\frac{C_H(S)}{C_H(S)}/\text{mM}$	$\frac{C_M(S)}{C_M(S)}/\text{mM}$	$\frac{C_A(S)}{C_A(S)}/\text{mM}$	$\frac{C_H(T)}{C_H(T)}/\text{mM}$	$\frac{C_A(T)}{C_A(T)}/\text{mM}$	$\frac{V_O}{V_O}/\text{ml}$
1	-	210.4	0	105.2	584	0	100.0
2	-	100.6	0	100.5	584	0	100.0
3	-	7.59	0	15.09	58.4	0	100.0
4	Pr	0.58	11.74	5.09	16.2	157.8	93.0
5	Pr	0.33	11.93	2.59	16.5	157.8	91.5
6	Pr	0.13	24.26	0	101.0	200.1	90.0
7	Pr	0.13	24.26	0	151.6	150.6	90.0
8	Pr	16.68	35.21	6.42	511.2	199.1	93.0
9	Eu	1.00	14.35	5.09	16.7	157.9	93.0
10	Eu	0.74	14.59	2.59	16.2	157.8	91.5
11	Eu	0.69	21.18	0	101.9	200.2	90.0
12	Eu	0.69	21.18	0	151.4	150.6	90.0
13	Eu	17.83	41.0	6.42	511.2	199.1	93.0
14	Ho	2.00	13.08	5.09	16.2	157.8	93.0
15	Ho	1.77	13.30	2.59	16.5	157.8	91.5
16	Ho	2.18	19.32	0	101.0	200.1	90.0
17	Ho	2.18	19.32	0	151.6	150.6	90.0
18	Ho	19.69	28.04	6.42	511.2	199.1	93.0
19	Lu	1.40	12.25	5.09	16.2	157.8	93.0
20	Lu	1.17	12.45	2.59	16.5	157.8	91.5
21	Lu	1.30	18.09	0	101.0	200.1	90.0
22	Lu	1.30	18.09	0	151.6	150.6	90.0
23	Lu	18.37	26.25	6.42	511.2	199.1	93.0

Table 2. The stability constants obtained from the potentiometric measurements. The errors are given as three standard deviations. Sig y is the error in the error-carrying variable $\frac{C_H}{C_A}$. The number of experimental points is denoted N.

Metal Constant	Pr	Eu	Ho	Lu	Sc
$\beta_{101} \times 10^{-6} \times M$	1.186 ± 0.036	2.87 ± 0.09	4.39 ± 0.13	11.59 ± 0.22	7000 ± 1900
$\beta_{102} \times 10^{-10} \times M^2$	4.71 ± 0.18	45.5 ± 1.9	92.8 ± 3.6	749 ± 17	$(1.15 \pm 0.34) \cdot 10^6$
$\beta_{103} \times 10^{-13} \times M^3$	5.91 ± 0.41	612 ± 44	1922 ± 120	1411 ± 75	-
$\beta_{111} \times 10^{-10} \times M^2$	5.51 ± 0.17	6.52 ± 0.17	4.75 ± 0.16	5.99 ± 0.10	38.6 ± 4.9
$\beta_{121} \times 10^{-12} \times M^3$	7.46 ± 0.58	8.10 ± 0.65	6.75 ± 0.68	5.10 ± 0.45	30 ± 30
<u>(Sig y)</u> $\times 10^3$	2.54	2.12	2.59	2.11	4.39
<u>N</u>	103	91	98	102	28

Table 3. The heats of dilution. In all the cases the S-solutions consisted of 1.00 M NaClO₄. $\underline{C}_M = 0$ in all T-solutions.

a) T: $\underline{C}_H = 0.584$ M, $\underline{C}_A = 0$. $\underline{V}_O = 100.0$ ml.

$\underline{v}/\text{ml}$, $\underline{Q}/\text{J}$: 3.00, -0.50; 6.00, -0.46; 9.00, -0.47;

9.00, -0.47; 12.00, -0.46; 15.00, -0.43; 18.00, -0.41

b) T: $\underline{C}_H = 0.0584$ M, $\underline{C}_A = 0$. $\underline{V}_O = 100.0$ ml.

$\underline{v}/\text{ml}$, $\underline{Q}/\text{J}$: 3.00, -0.10; 6.00, -0.11; 9.00, -0.13; 12.00, -0.13.

c) T: $\underline{C}_H = 0.0167$ M, $\underline{C}_A = 0.1579$ M. $\underline{V}_O = 90.0$ ml.

$\underline{v}/\text{ml}$, $\underline{Q}/\text{J}$: 3.00, -0.11; 6.00, -0.03; 9.00, -0.02; 12.00, -0.01;

15.00, -0.01; 18.00, -0.03; 21.00, -0.03; 24.00, -0.02; 27.00, -0.02

d) T: $\underline{C}_H = 0.0167$ M, $\underline{C}_A = 0.1579$ M. $\underline{V}_O = 90.0$ ml.

$\underline{v}/\text{ml}$, $\underline{Q}/\text{J}$: 1.50, -0.07; 4.50, -0.05.

e) T: $\underline{C}_H = 0.1019$ M, $\underline{C}_A = 0.2002$ M. $\underline{V}_O = 90.0$ ml.

$\underline{v}/\text{ml}$, $\underline{Q}/\text{J}$: 3.00, 0.20; 6.00, 0.18; 9.00, 0.16; 12.00, 0.15;

15.00, 0.12; 18.00, 0.13; 21.00, 0.13; 24.00, 0.10; 27.00, 0.08.

f) T: $\underline{C}_H = 0.1514$ M, $\underline{C}_A = 0.1506$ M. $\underline{V}_O = 90.0$ ml.

$\underline{v}/\text{ml}$, $\underline{Q}/\text{J}$: 3.00, 0.10; 6.00, 0.12; 9.00, 0.12; 12.00, 0.12;

15.00, 0.10; 18.00, 0.09; 21.00, 0.08.

g) T: $\underline{C}_H = 0.5112$ M, $\underline{C}_A = 0.1991$ M. $\underline{V}_O = 90.0$ ml.

$\underline{v}/\text{ml}$, $\underline{Q}/\text{J}$: 3.00, -1.62; 6.00, -0.83; 9.00, -0.61; 12.00, -0.49;

15.00, -0.42; 18.00, -0.38; 21.00, -0.35.

Table 4. Corresponding values of v/ml , $(Q_{corr} \cdot 100)/J$ and $(Q_{corr,calc} - Q_{corr,obs}) \times 100 \times J^{-1}$ from the calorimetric titrations.

Series 1: 3.00, 586, -1; 6.00, 568, -4; 9.00, 534, -3;
12.00, 483, -2; 15.00, 425, -10.

Series 2: 3.00, 597, -9; 6.00, 594, -6; 9.00, 587, 4; 12.00, 591, 1;
15.00, 580, 10; 18.00, 567, 15.

Series 3: 3.00, 627, 0; 6.00, 629, -3; 9.00, 629, -3; 12.00, 626, 2.

Series 4: 3.00, 186, -10; 6.00, 239, -6; 9.00, 293, 3; 12.00, 334, -6;
15.00, 353, 0; 18.00, 323, -1; 21.00, 208, 0; 24.00, 96, -4.

Series 5: 3.00, 178, -15; 6.00, 209, -11; 9.00, 268, 1; 12.00, 315, -3.
15.00, 345, -3; 18.00, 342, 5; 21.00, 275, -1; 24.00, 141, 4.

Series 6: 3.00, 93, 4; 6.00, 81, 0; 9.00, 93, 5; 12.00, 107, 8;
15.00, 121, 12; 18.00, 140, 11; 21.00, 154, 15;
24.00, 175, 10; 27.00, 195, 3.

Series 7: 3.00, -117, -2; 6.00, -98, -5; 9.00, -94, 1; 12.00, -88, 3;
15.00, -84, 7; 18.00, -79, 9; 21.00, -74, 10.

Series 8: 3.00, -24, -17; 6.00, -17, -1; 9.00, -16, 8; 12.00, -10, 7;
15.00, -8, 8; 18.00, -5, 7.

Series 9: 3.00, 214, -16; 6.00, 290, -16; 9.00, 391, 3; 12.00, 487, 11;
15.00, 572, -7; 18.00, 632, -13; 21.00, 659, -3;
24.00, 647, 3; 27.00, 350, 16.

Series 10: 3.00, 189, -11; 6.00, 247, -17; 9.00, 339, -6;
12.00, 447, 7; 15.00, 536, 0; 18.00, 609, -14;
21.00, 654, -11; 24.00, 667, -3; 27.00, 551, 17.

Series 11: 3.00, 228, 8; 6.00, 81, 7; 9.00, 107, 10;
12.00, 140, 12; 15.00, 171, 19; 18.00, 214, 16;
21.00, 254, 14; 24.00, 287, 15; 27.00, 330, 0.

Series 12: 3.00, -100, -5; 6.00, -112, -7; 9.00, -114, 2;
12.00, -108, 5; 15.00, -100, 6; 18.00, -94, 3;
21.00, -87, 8.

Series 13: 3.00, -39, -18; 6.00, -23, -8; 9.00, -29, 10;
12.00, -20, 8; 15.00, -20, 12; 18.00, -13, 8.

Series 14: 3.00, -5, -15; 6.00, 77, -17; 9.00, 223, -3;
12.00, 405, -3; 15.00, 622, -10; 18.00, 855, -3;
21.00, 1028, 2.

Series 15: 3.00, -18, -11; 6.00, 24, -14; 9.00, 142, -10;
12.00, 308, 1; 15.00, 501, -4; 18.00, 732, -5;
21.00, 941, 9; 24.00, 1052, 3; 27.00, 521, -5.

Series 16: 3.00, 502, 17; 6.00, -42, 3; 9.00, -37, 7;
12.00, -11, 14; 15.00, 39, 25; 18.00, 69, 26;
21.00, 125, 17; 24.00, 175, 19.

Series 17: 3.00, -49, -3; 6.00, -107, -6; 9.00, -120, -5;
12.00, -123, 0; 15.00, -122, 5; 18.00, -116, 5;
21.00, -116, 13.

Series 18: 3.00, -25, -19; 6.00, -20, -3; 9.00, -24, 11;
12.00, -15, 7; 15.00, -13, 8; 18.00, -11, 9.

Series 19: 3.00, 83, -12; 6.00, 165, -10; 9.00, 270, -1;
12.00, 351, -7; 15.00, 623, -5; 18.00, 869, 3;
21.00, 705, -9.

Series 20: 3.00, 67, -12; 6.00, 119, -14; 9.00, 218, -5;
12.00, 312, -3; 15.00, 408, -5; 18.00, 816, 13;
21.00, 819, -5.

Series 21: 3.00, 278, 3; 6.00, 6. 2; 9.00, 25, 9; 12.00, 59, 13;
15.00, 91. 22; 18.00, 135, 18; 21.00, 173, 15; 24.00, 205, 10.

Series 22: 3.00, -137, -3; 6.00, -177, -4; 9.00, -182, 5; 12.00, -174, 7;
15.00, -164, 9; 18.00, -153, 9; 21.00, -146, 12.

Series 23: 3.00, -22, -20; 6.00, -20, 0; 9.00, -19, 8;
12.00, -10, 5; 15.00, -10, 8; 18.00, -11, 11.

Table 5. The enthalpy changes obtained from the calorimetric titrations and the corresponding entropy changes. The quantities ΔH° are divided by $\text{kJ} \cdot \text{mol}^{-1}$; the quantities ΔS° are divided by $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. The errors are given as three standard deviations. ΔH° is equal to the standard deviation in the measured $\Delta_{\text{comp}}^\circ$ values.

	$\frac{-\Delta H^\circ}{011}$	$\frac{-\Delta H^\circ}{021}$	$\frac{-\Delta H^\circ}{031}$	$\frac{\Delta S^\circ}{011}$	$\frac{\Delta S^\circ}{021}$	$\frac{\Delta S^\circ}{031}$	$\frac{\Delta H^\circ}{J}$
Promotion	35.64 ± 0.72	39.04 ± 0.72	43.22 ± 0.73	59	97	119	0.084

Metal	$\frac{-\Delta H^\circ}{101}$	$\frac{-\Delta H^\circ}{102}$	$\frac{-\Delta H^\circ}{103}$	$\frac{-\Delta H^\circ}{111}$	$\frac{-\Delta H^\circ}{121}$
Pr	3.63 ± 0.27	11.04 ± 0.35	20.27 ± 0.46	31.46 ± 0.78	46.04 ± 1.90
Eu	3.72 ± 0.39	16.51 ± 0.43	33.15 ± 0.54	30.82 ± 1.20	44.07 ± 2.33
Ho	-1.47 ± 0.40	6.15 ± 0.55	14.29 ± 0.62	28.59 ± 1.53	46.37 ± 3.88
Lu	0.55 ± 0.38	8.94 ± 0.43	12.36 ± 0.60	27.98 ± 1.90	49.48 ± 4.58

Metal	$\frac{\Delta H^\circ}{101}$	$\frac{\Delta H^\circ}{102}$	$\frac{\Delta H^\circ}{103}$	$\frac{\Delta S^\circ}{111}$	$\frac{\Delta S^\circ}{121}$	$\frac{\Delta H^\circ}{J}$
Pr	104	167	194	100	92	0.080
Eu	111	166	191	104	99	0.115
Ho	132	202	197	108	90	0.121
Lu	133	217	200	109	77	0.107

Ref. E

Thermodynamic Properties of Rare Earth Complexes

XV. Free Energy, Enthalpy and Entropy Changes for the Formation of Rare Earth(III)-Ethylenediamine-N,N'-diacetate Complexes.

Göran Gårdhammar

Division of Physical Chemistry 1, Chemical Center,
University of Lund, P.O.B. 740, S-220 07 Lund 7, Sweden.

The stability constants for the complexes MA^+ , MA_2^- , MHA^{2+} and MH_2A^{3+} (where M denotes a rare earth metal, H_2A ethylenediamine-N,N'-diacetic acid) have been determined. The metals investigated are La, Nd, Sm, Tb, Er and Yb. The changes in enthalpy and entropy for the formation of the complexes MA^+ and MA_2^- were also determined. In the latter investigation the enthalpies of complexation of Gd and Dy were also determined. The corresponding stability constants were estimated from previous determinations. All measurements were performed at 25.0 °C in a medium with ionic strength 1.0 M using sodium perchlorate as the neutral salt.

Several studies of thermodynamic properties for rare earth carboxylate complexes have been reported in the previous parts of this series.¹⁻¹³ For many ligands, viz. diglycolate,^{1,2} dipicolinate,^{2,14} iminodiacetate^{10,13} and thiodiacetate,¹⁵ there is a similarity in the variation of the enthalpy and entropy changes for the various complex formation reactions through the lanthanoid series. In the present study the ligand ethylenediamine-N,N'-diacetate, $^-\text{OOC}-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{COO}^-$, is included. Reasons for the choice of this four-dentate ligand where the following:

- a) We wanted to investigate a ligand with a geometry different from previously studied ligands in order to investigate how such a change affects the thermodynamic quantities studied.
- b) We were interested to know if metal complexes were formed with HA^- and H_2A and to decide whether these complexes are chelates or not.

The stability constants for the complexes MA^+ and MA_2^- have been determined before.^{16,17} This study will extend the earlier measurements to include investigations of the corresponding enthalpy and entropy values for La, Nd, Sm, Gd, Tb, Dy, Er and Yb. We have also made new determinations of the stability constants for most of the above systems. (The exceptions are Gd and Dy.)

All measurements have been performed at 25.0 °C in a medium with ionic strength 1.0 M using sodium perchlorate as the neutral salt. The stability constants were determined by a potentiometric standard method, viz. emf-measurements of the hydrogen ion concentration. The enthalpy changes were obtained by calorimetric titrations.

The symbols used are given in Ref. 9 and 13. The calculations are the same as described previously.^{10,13}

EXPERIMENTAL

Ethylenediamine-N,N'-diacetic acid (La Mont Laboratories) was purified by repeated recrystallizations from water. The purity was determined by complexometric titration with copper(II) using murexide as the indicator. The experimental formula weight was 176.3. The theoretical value is 176.17.

All other experimental details have been given before.¹³ The volume of the inner reaction vessel in the calorimetric measurements was about 100 ml. The volume V_0 and the volumes of added T-solution in the various titrations are given in Tables 1 and 2.

RESULTS

Determination of stability constants. The titration series for the proton and Sm systems are given in Tables 1 and 2. The Sm system is used as a model for the experimental behaviour of the other systems. Stability constants obtained from the Sm system were also calculated by using only two titration series (7 and 12). These series have stoichiometric compositions, which are similar to those used in the other lanthanoid systems investigated. This latter set of constant values were then used when the other thermodynamic properties were calculated. Such a selection of the experimental material is discussed in Ref. 13, p. 4-5.

The experimental data could be described rather well by assuming the formation of the complexes MA^+ , MA_2^- and MH_2A^{3+} . However, the existence of the complex MHA^{2+} seems rather probable for chemical reasons^{9,10,13,15} and the final least-squares refinements have been made with this species included. The stability

constants obtained from the different systems are given in Table 3. (For the Sm systems two different sets are given, corresponding to the complete experimental material and the two selected series.) It should be observed that the presence of the complex MHA^{2+} cannot unequivocally be decided from the experimental data. This species, if existing, is never present with more than a few per cent (2 % in the Sm system) of the total metal concentration in the solutions studied. Sig y and the other stability constants obtained from a calculation with MHA^{2+} excluded remain practically unchanged.

Determination of enthalpy changes. The experimental Q -values are positive for exothermal and negative for endothermal reactions.

The heats of dilution of perchloric acid have been given before.¹³ The heats of dilution of the other T-solutions (approximately Na_2A -solutions) vary between 0.10 and 0.01 J per addition of 2.00 ml. The experimental data for the protonation and metal complexation reactions are collected in Tables 4 and 5. Values of the quantity ΔQ (Cf. Ref. 13) have also been included in Table 5. The various molar changes are given in Table 6 with their estimated errors. The least-squares refinement of most of the calorimetric data have been made by using the stability constants β_{011} , β_{021} , β_{101} and β_{102} given in Table 3. The constants β_{101} and β_{102} for the Gd- and Dy-systems have been estimated from the values in Table 3 and the values obtained by Thompson.¹⁶

These results are:

$$\begin{aligned}\beta_{101} &= 1.55 \cdot 10^8 \text{ M}^{-1}; \quad \beta_{102} = 3.2 \cdot 10^{14} \text{ M}^{-2} \text{ (Gd)} \quad \text{and} \\ \beta_{101} &= 2.7 \cdot 10^8 \text{ M}^{-1}; \quad \beta_{102} = 2.7 \cdot 10^{15} \text{ M}^{-2} \text{ (Dy)}\end{aligned}$$

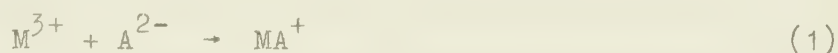
The neutralization reaction $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$ has been added in the final computations but no hydroxo complexes have been taken into account. (Cf. Ref. 13, p. 6). The corresponding

corrections are of the same magnitude as those described for the iminodiacetate systems.¹³

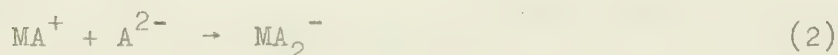
DISCUSSION

The stability constants obtained in this study agree well with earlier results.^{16,17} However, no acid complexes have been described so far. This is not especially surprising as the previous investigators have not studied the complexation reactions in the region of high hydrogen ion concentration. If we exclude the titration data from our most acid solutions we find that the experimental material can well be described by only two complexes, viz. MA^+ and MA_2^- . The following results are obtained from series 7 in the Sm system: $\beta_{101} = (1.24 \pm 0.02) \cdot 10^8 \text{ M}^{-1}$; $\beta_{102} = (1.87 \pm 0.05) \cdot 10^{14} \text{ M}^{-2}$, $\text{sig}_y = 1.94 \cdot 10^{-3}$ (21 experimental points).

Figures 1-4 show the entropy (ΔS_1^0 , ΔS_2^0) and enthalpy values (ΔH_1^0 , ΔH_2^0) for the reactions

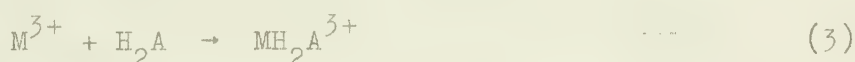


and



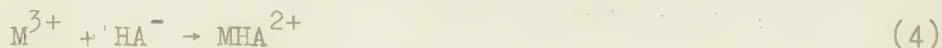
as a function of the atomic number. The values from the corresponding iminodiacetate¹³ and dipicolinate² systems are also represented in the figures. It is clear that the same type of variations as found for many ligands⁴ is also obtained for ethylenediaminediacetate. The similarities are especially conspicuous for the first reaction step.

The stability constants for the reaction



decreases in the end of the lanthanoid series with increasing atomic number. The same trend has been found for other ligands, i.e. acetate,³ bimalonate,⁹ bithiodiacetate¹⁵ and the two acid iminodiacetate ligands.¹³ However, there is no increase in stability ($-\Delta G^0$) in the beginning of the lanthanoid series for reaction (3). An increasing stability from La through about Eu is otherwise the normal behaviour for most ligands investigated. The magnitude of the stability constants for reaction (3) ($11-18 \text{ M}^{-1}$) seems to indicate that H_2A is coordinated as an unidentate ligand. (Cf. Ref. 10, p. 1406). The acid H_2A probably exists mainly in the form $^-\text{OOC}-\text{CH}_2-\text{NH}_2^+-\text{CH}_2-\text{CH}_2-\text{NH}_2^+-\text{CH}_2-\text{COO}^-$. This assumption is also supported by the high values of $-\Delta H_{0q1}^0$ (cf. Table 6).

The values of the stability constants for the reaction



are too uncertain to allow a discussion of the variation through the lanthanoid series. The value of the constant has the same magnitude for all the investigated central ions, e.g. 50 (La) and 300 (Tb). This fact is an indication that the existence of the complex MHA^{2+} is real. However, the uncertainty in the results makes it very hard to decide which type of coordination that is most probable. The values are perhaps high enough to assume a bidentate coordination to oxygen and nitrogen. (Cf Ref. 10, p. 1406.)

Acknowledgement. We are indebted to Professor Ido Leden for valuable comments on the above subject. This investigation has partly been supported by a grant from the Swedish Natural Science Research Council.

REFERENCES

1. Grenthe, I. and Tobiasson, I. Acta Chem. Scand. 17 (1963) 2101.
2. Grenthe, I. Acta Chem. Scand. 17 (1963) 2487.
3. Grenthe, I. Acta Chem. Scand. 18 (1964) 283.
4. Grenthe, I. Acta Chem. Scand. 18 (1964) 293.
5. Grenthe, I. and Williams, D.R. Acta Chem. Scand. 21 (1967) 347.
6. Grenthe, I., Gårdhammar, G. and Runderantz, E. Acta Chem. Scand. 23 (1969) 93.
7. Grenthe, I. and Hansson, E. Acta Chem. Scand. 23 (1969) 611.
8. Gårdhammar, G. Acta Chem. Scand. 25 (1971) 158.
9. Dellien, I. and Grenthe, I. Acta Chem. Scand. 25 (1971) 1387.
10. Grenthe, I. and Gårdhammar, G. Acta Chem. Scand. 25 (1971) 1401.
11. Grenthe, I. and Ots, H. Acta Chem. Scand. 26 (1972). (In press.)
12. Grenthe, I. and Ots, H. Acta Chem. Scand. 26 (1972). (In press.)
13. Grenthe, I. and Gårdhammar, G. Acta Chem. Scand. (In press.)
14. Grenthe, I. J. Am. Chem. Soc. 83 (1961) 360.
15. Dellien, I., Grenthe, I. and Hessler, G. To be published.
16. Thompson, L.C. J. Inorg. Nucl. Chem. 24 (1962) 1083.
17. Sevost'yanova, N.I., Martynenko, L.I. and Spitsyn, V.I. Russ. J. Inorg. Chem. 15 (5) (1970) 633.

Table 1. Composition of various S- and T-solutions in the potentiometric titrations. Series 1-6 represent the proton system, series 7-12 the Sm system. $\bar{C}_M(T) = \bar{C}_A(T) = 0$ in all cases.

Series	$\bar{C}_H(S)/mM$	$\bar{C}_M(S)/mM$	$\bar{C}_A(S)/mM$	$\bar{C}_H(T)/mM$	$\bar{V}_O/ml$
1	19.34	0	9.67	-24.55	20.00
2	40.7	0	20.36	-99.1	20.00
3	79.6	0	39.8	-99.0	20.00
4	19.34	0	9.67	116.1	25.00
5	40.7	0	20.36	116.1	20.00
6	79.6	0	39.8	116.1	15.00
7	62.2	9.50	30.78	-148.5	20.00
8	100.7	19.00	49.7	-149.0	20.00
9	79.8	19.00	39.9	232.8	20.00
10	31.47	13.30	15.30	232.8	20.00
11	42.0	19.00	20.36	232.8	20.00
12	41.6	9.50	20.49	232.8	20.00

Table 2. Corresponding values of v/ml , $-\log(h/M)$ and $(C_H(\text{calc}) - C_H(\text{exp}))C_A^{-1} \times 10^4$ for potentiometric measurements. Every second experimental point in each series from the proton and Sm systems is represented. (Cf. Table 1.)

Series 1: 0.40, 5.450, 6; 0.70, 5.699, 19; 1.10, 5.920, 22; 1.80, 6.179, 38; 2.70, 6.425, 40; 3.70, 6.657, 32; 4.75, 6.894, 10; 5.80, 7.159, -13; 6.60, 7.428, -48; 7.25, 7.758, -77; 8.60, 8.767, -53; 9.20, 9.020, -22.

Series 2: 0.20, 5.426, 19; 0.35, 5.678, 28; 0.55, 5.898, 32; 0.90, 6.155, 47; 1.30, 6.375, 43; 1.80, 6.601, 44; 2.40, 6.858, 30; 2.95, 7.115, 18; 3.35, 7.355, -13; 3.65, 7.599, -26; 3.90, 7.896, -35; 4.05, 8.143, -46; 4.20, 8.397, -44; 4.40, 8.667, -31; 4.65, 8.905, -9; 5.00, 9.144, 17; 5.45, 9.377, 42; 6.00, 9.615, 74.

Series 3: 0.40, 5.448, -5; 0.65, 5.668, -8; 1.00, 5.874, -11; 1.65, 6.131, -10; 2.50, 6.375, -21; 3.50, 6.606, -22; 4.70, 6.867, -23; 5.80, 7.132, -37; 6.60, 7.377, -46; 7.15, 7.611, -56; 7.60, 7.881, -58; 8.00, 8.209, -55; 8.40, 8.535, -52; 8.85, 8.796, -33; 9.50, 9.058, -16; 10.40, 9.318, -2; 11.70, 9.612, 33.

Series 4: 0.20, 3.536, -11; 0.42, 3.202, -9; 0.72, 2.952, -8; 1.20, 2.703, 23; 2.00, 2.448, 0; 3.15, 2.211, -48; 5.00, 1.968, -119; 8.10, 1.723, 119.

Series 5: 0.20, 3.682, 6; 0.40, 3.374, 9; 0.70, 3.117, 12; 1.15, 2.877, 38; 1.90, 2.627, 31; 3.00, 2.384, 0; 4.50, 2.150, -5; 6.90, 1.897, 6.

Series 6: 0.20, 3.802, 0; 0.40, 3.503, 1; 0.68, 3.263, 4; 1.15, 3.014, 18; 1.80, 2.794, 22; 2.80, 2.563, 28; 4.30, 2.321, -11; 6.30, 2.083, -19; 9.10, 1.841, 5.

Series 7: 0.20, 4.319, -14; 0.45, 4.549, -23; 0.95, 4.796, -38; 1.67, 5.053, -58; 2.40, 5.327, -28; 3.00, 5.595, 4; 3.65, 5.861, -14; 4.50, 6.155, -21; 5.28, 6.458, -25; 5.80, 6.750, -11; 6.20, 7.041, -19.

Series 8: 0.00, 3.797, 2; 0.20, 4.066, -2; 0.49, 4.301, 9; 1.05, 4.530, 25; 2.06, 4.767, 32; 2.40, 5.011, 22; 4.70, 5.266, 37; 5.80, 5.533, 31; 7.00, 5.808, 1; 8.30, 6.069, 4; 9.60, 6.356, 15; 10.55, 6.650, 19; 11.10, 6.917, 16.

Series 9: 0.00, 4.001, 14; 0.20, 3.521, 18; 0.40, 3.236, 24; 0.67, 3.006, 25; 1.08, 2.779, 31; 1.70, 2.553, 11; 2.60, 2.321, -13; 3.90, 2.074, -17; 5.70, 1.819, -17.

Series 10: 0.00, 3.628, 2; 0.10, 3.276, 5; 0.20, 3.070, 20; 0.40, 2.815, 30; 0.69, 2.583, 18.

Series 11: 0.00, 3.555, -4; 0.10, 3.286, -15; 0.24, 3.051, -7; 0.46, 2.821, -7;

Series 12: 0.00, 3.834, 4; 0.10, 3.442, 17; 0.20, 3.220, 28; 0.40, 2.955, 30; 0.67, 2.732, 18; 1.10, 2.493, 7; 1.70, 2.263, -54; 2.60, 2.015, -11.

Table 3. Stability constants obtained from the potentiometric measurements. Sig y is the error in the error-carrying variable, C_H/C_A . The number of experimental points is denoted N.

Metal	$\beta_{101} \times 10^{-6} \text{ xM}$	$\beta_{102} \times 10^{-11} \text{ xM}^2$	$\beta_{121} \times 10^{-17} \text{ xM}^3$	$\beta_{111} \times 10^{-11} \text{ xM}^2$	$(\text{Sig } y) \cdot 10^3$	<u>N</u>
La	9.02±0.28	3.57±0.18	4.53±0.39	2.5±2.3	3.81	36
Nd	94.7 ±1.7	388±10	3.98±0.23	5.5±1.1	2.68	39
Sm	181.7 ±1.9	2750±40	3.98±0.10	7.1±0.3	2.24	97
Sm	175.8 ±4.4	2620±80	4.01±0.27	6.0±3.2	1.73	37
Tb	183.4 ±5.9	(1.119±0.040)·10 ⁴	4.50±0.35	14±6	2.27	38
Er	322 ±7	(8.68 ±0.23)·10 ⁴	3.69±0.06	11±7	2.12	39
Yb	672 ±24	(8.65 ±0.28)·10 ⁵	2.83±0.24	12±13	2.10	38

$$\beta_{011} = (4.95 \pm 0.07) \times 10^9 \text{ M}^{-1}$$

$$\beta_{021} = (2.574 \pm 0.041) \times 10^{16} \text{ M}^{-2}$$

$$\beta_{031} = (6.02 \pm 0.12) \times 10^{18} \text{ M}^{-3}$$

$$\beta_{041} = (2.775 \pm 0.054) \times 10^{20} \text{ M}^{-4}$$

Table 4. Composition of the various S- and T-solutions in the calorimetric titrations. Series 1-2 represent the proton system. $C_M(T) = 0$ in all cases.

Series	Metal	$C_H(S)/mM$	$C_M(S)/mM$	$C_A(S)/mM$	$C_H(T)/mM$	$C_A(T)/mM$	V_O/ml
1	-	6.80	0	16.13	59.8	0	86.0
2	-	23.46	0	20.19	59.8	0	80.0
3	La	0.53	9.40	1.284	9.30	104.0	81.0
4	La	0.64	9.29	2.537	9.30	104.0	82.0
5	Nd	0.37	10.27	1.284	8.60	104.0	81.0
6	Nd	0.47	10.15	2.537	8.60	104.0	82.0
7	Sm	0.72	9.38	1.284	8.60	104.0	81.0
8	Sm	0.81	9.27	2.537	8.60	104.0	82.0
9	Gd	0.18	9.67	1.284	9.30	104.0	81.0
10	Gd	0.30	9.55	2.537	9.30	104.0	82.0
11	Tb	0.52	10.00	1.284	9.30	104.0	81.0
12	Tb	0.43	9.88	2.537	9.30	104.0	82.0
13	Dy	0.74	9.28	1.283	8.70	103.9	81.0
14	Dy	0.84	9.17	2.534	8.70	103.9	82.0
15	Er	0.38	9.62	1.284	8.60	104.0	81.0
16	Er	0.48	9.50	2.537	8.60	104.0	82.0
17	Yb	1.43	9.96	1.284	9.30	104.0	81.0
18	Yb	1.52	9.83	2.537	9.30	104.0	82.0

Table 5. Corresponding values of v/ml , $(Q_{corr,calc} \cdot 100)/J$ and $(Q_{corr,calc} - Q_{corr,obs}) \times 100 \times J^{-1}$ for the calorimetric titrations.

Series 1: 2.00, 454, -3; 4.00, 452, -2; 6.00, 448, 1; 8.00, 449, -1;
10.00, 448, 0; 12.00, 444, 3; 14.00, 442, 4.

Series 2: 2.00, 442, 3; 4.00, 449, -4; 6.00, 450, -5; 8.00, 446, -1;
10.00, 448, -3; 12.00, 446, -1; 14.00, 442, 3; 16.00, 441, 4.

Series 3: 2.00, 95, 0; 4.00, 92, -3; 6.00, 97, -1; 8.00, 123, -5;
10.00, 159, -8; 12.00, 162, -5; 14.00, 142, 12.

Series 4: 2.00, 92, -1; 4.00, 90, 5; 6.00, 107, -5; 8.00, 147, -9;
10.00, 163, -7; 12.00, 154, 4; 14.00, 128, 14.

Series 5: 2.00, 217, -5; 4.00, 208, 3; 6.00, 203, 5; 8.00, 193, 0;
10.00, 166, 5; 12.00, 162, 4; 14.00, 164, -1; 16.00, 160, -5.

Series 6: 2.00, 212, -1; 4.00, 212, -2; 6.00, 204, 0; 8.00, 181, -2;
10.00, 168, 0; 12.00, 165, 0; 14.00, 161, -4.

Series 7: 2.00, 250, -4; 4.00, 248, -3; 6.00, 245, 0; 8.00, 241, 5;
10.00, 248, 0; 12.00, 246, -1; 14.00, 242, -2.

Series 8: 2.00, 248, -2; 4.00, 245, 2; 6.00, 242, 3; 8.00, 239, 9;
10.00, 244, 0; 12.00, 240, -4.

Series 9: 2.00, 185, -1; 4.00, 189, -1; 6.00, 202, -5; 8.00, 247, 9;
10.00, 281, 11; 12.00, 307, -6; 14.00, 315, -20.

Series 10: 2.00, 177, 5; 4.00, 192, -4; 6.00, 214.2; 8.00, 257, 17;
10.00, 292, 7; 12.00, 309, -10.

Series 11: 2.00, 104, -1; 4.00, 123, -7; 6.00, 145, 1; 8.00, 199, 10;
10.00, 267, 11; 12.00, 316, -5; 14.00, 335, -15.

Series 12: 2.00, 111, -1; 4.00, 112, -3; 6.00, 170, 3; 8.00, 232, 14;
10.00, 296, 4; 12.00, 328, -8.

Series 13: 2.00, 88, -6; 4.00, 106, -6; 6.00, 135, 4; 8.00, 189, 14;
10.00, 253, 11; 12.00, 297, -3; 14.00, 314, -21.

Series 14: 2.00, 97, -8; 4.00, 121, -5; 6.00, 157, 11; 8.00, 222, 14;
10.00, 279, 4; 12.00, 309, -10.

Series 15: 2.00, 45, -1; 4.00, 66, -1; 6.00, 101, -1; 8.00, 144, 3;
10.00, 185, 8; 12.00, 222, 4; 14.00, 244, -6.

Series 16: 2.00, 54, -1; 4.00, 85, -4; 6.00, 123, -1; 8.00, 164, 7;
10.00, 206, 5; 12.00, 232, 2; 14.00, 235, -15.

Series 17: 2.00, 85, 3; 4.00, 120, -5; 6.00, 151, -4; 8.00, 185, -4;
10.00, 214, 1; 12.00, 247, 1; 14.00, 276, 7.

Series 18: 2.00, 96, 5; 4.00, 129, 1; 6.00, 165, -2; 8.00, 199, -1;
10.00, 231, 1; 12.00, 260, 3; 14.00, 290, -4.

Table 6. The enthalpy changes obtained from the calorimetric titrations and the corresponding entropy changes. The quantities ΔH° are divided by $\text{kJ}\cdot\text{mole}^{-1}$; the quantities ΔS° are divided by $\text{J}\cdot\text{mole}^{-1}\cdot\text{K}^{-1}$. The errors are given as three standard deviations. Sig Q is equal to the standard deviation in the measured Q_{corr} -values.

	$-\frac{\Delta H^\circ}{Q_{011}}$	$-\frac{\Delta H^\circ}{Q_{021}}$	$\frac{\Delta S^\circ}{Q_{011}}$	$\frac{\Delta S^\circ}{Q_{021}}$	<u>Sig Q/J</u>
Protonation	37.27±0.36	74.50±0.46	61	64	0.035
Metal	$-\frac{\Delta H^\circ}{101}$	$-\frac{\Delta H^\circ}{102}$	$\frac{\Delta S^\circ}{101}$	$\frac{\Delta S^\circ}{102}$	<u>Sig Q/J</u>
La	4.69±0.50	13.22±0.66	117	177	0.076
Nd	10.50±0.18	19.21±0.24	117	196	0.029
Sm	12.20±0.36	25.17±0.47	117	192	0.055
Gd	8.99±0.68	24.95±0.87	127	194	0.101
Tb	4.76±0.58	22.12±0.70	142	214	0.082
Dy	3.54±0.85	19.82±0.97	148	229	0.114
Er	1.40±0.47	14.39±0.49	158	257	0.059
Yb	3.24±0.35	19.15±0.33	158	260	0.041

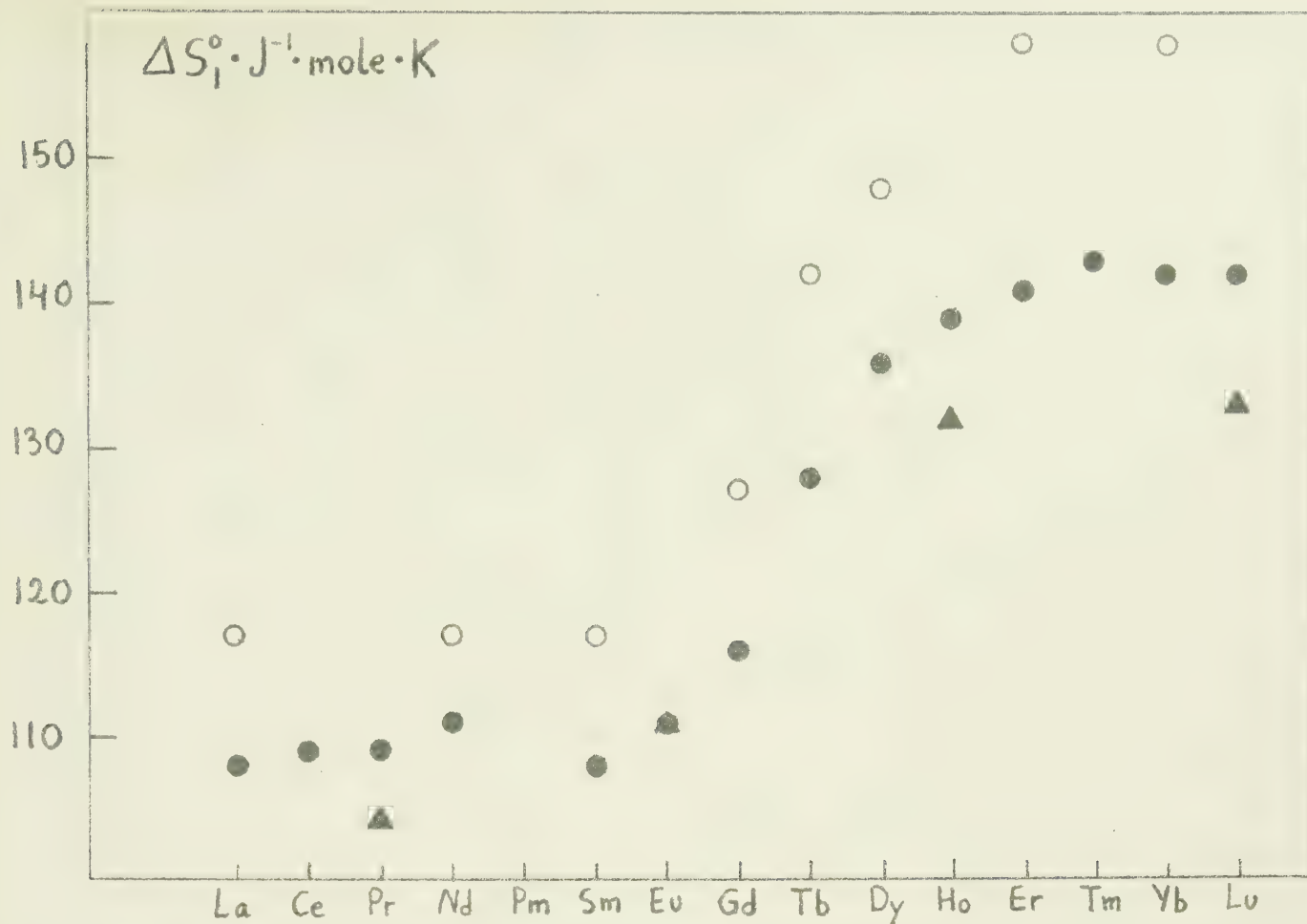


Fig. 1. ●=dipicolinate, ○=ethylenediaminediacetate, ▲=iminodiacetate

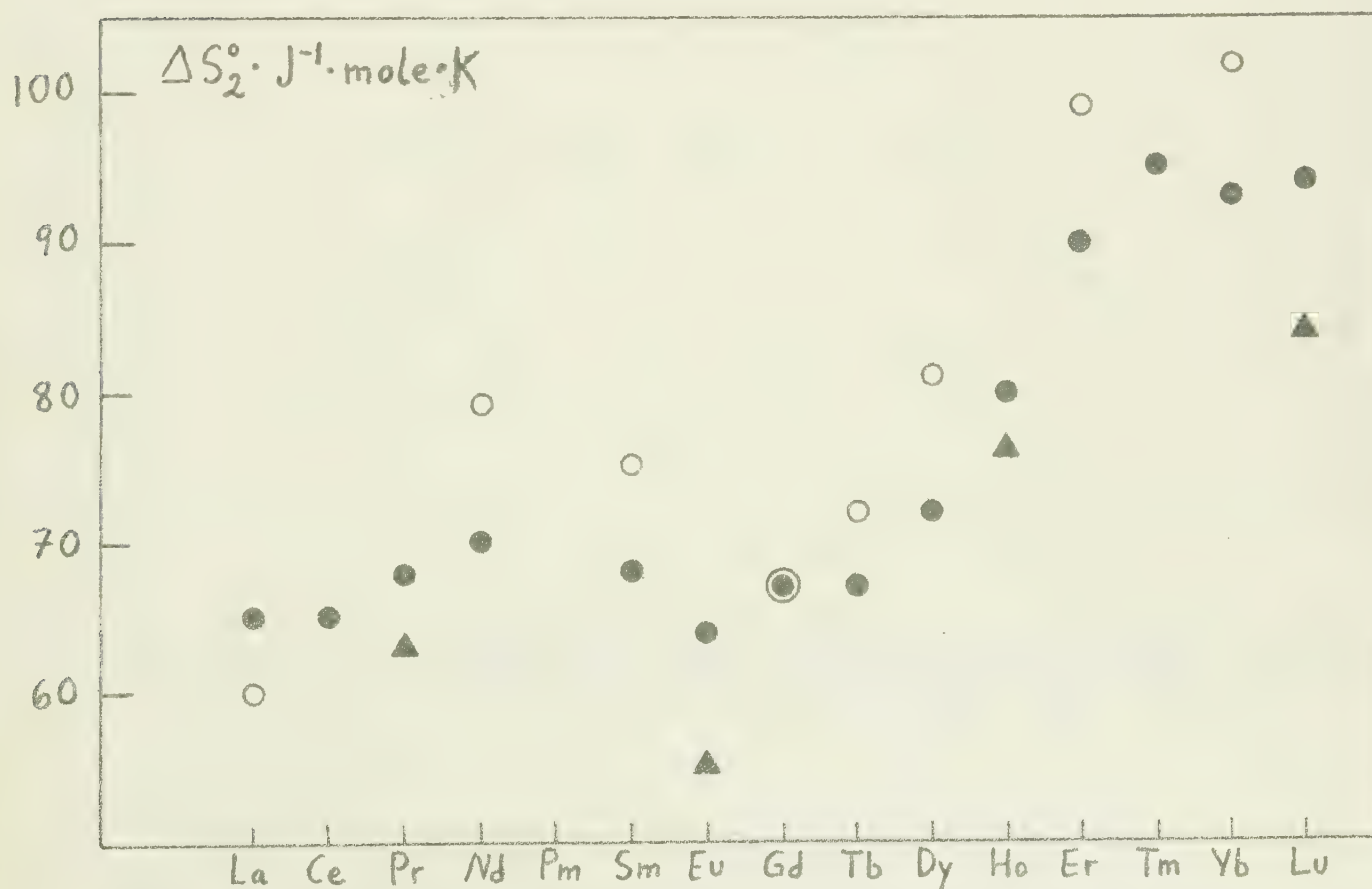


Fig. 2. ●=dipicolinate, ○=ethylenediaminediacetate, ▲=iminodiacetate

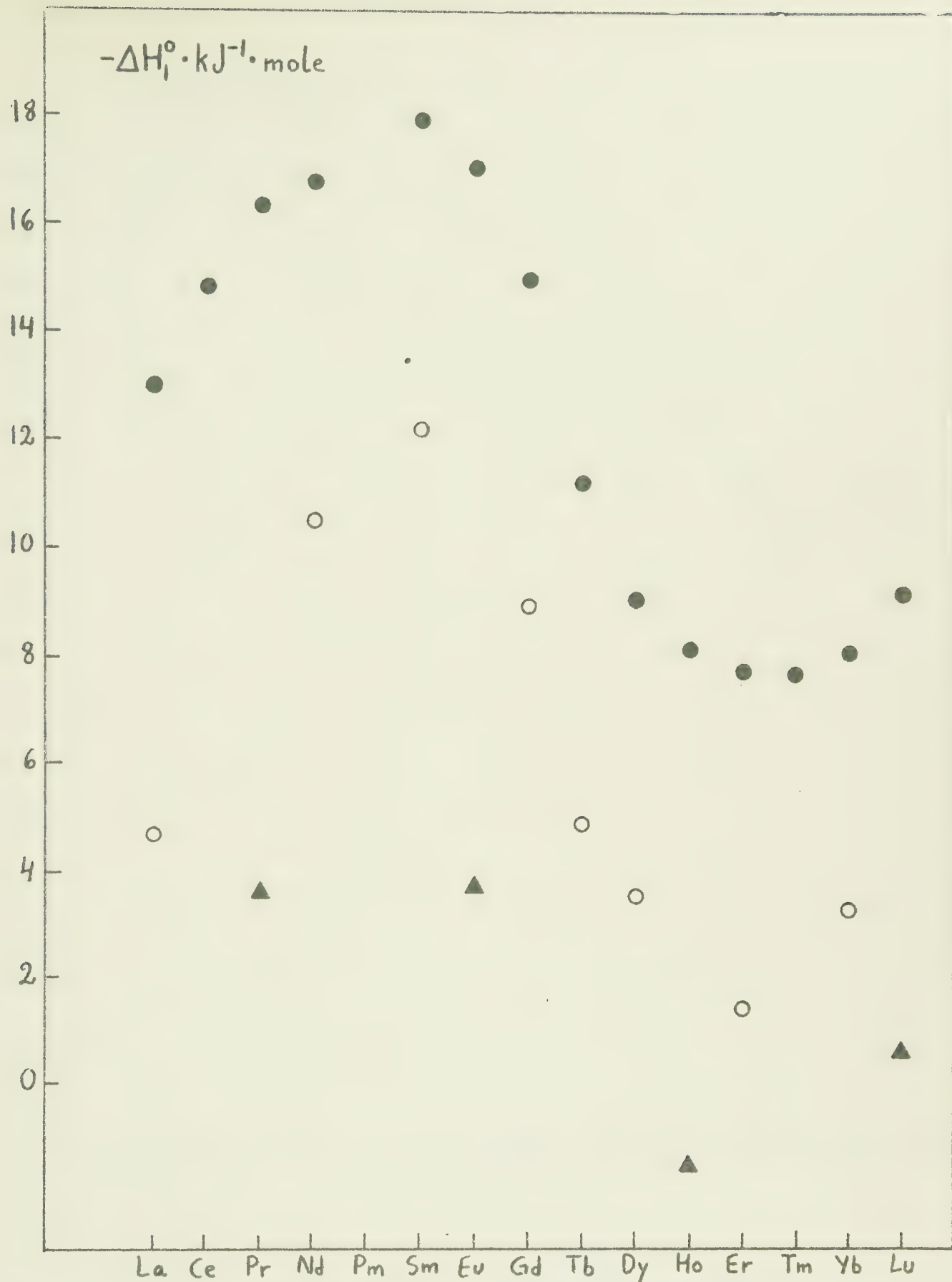


Fig. 3

●=dipicolinate, ○=ethylenediaminediacetate,

▲=iminodiacetate

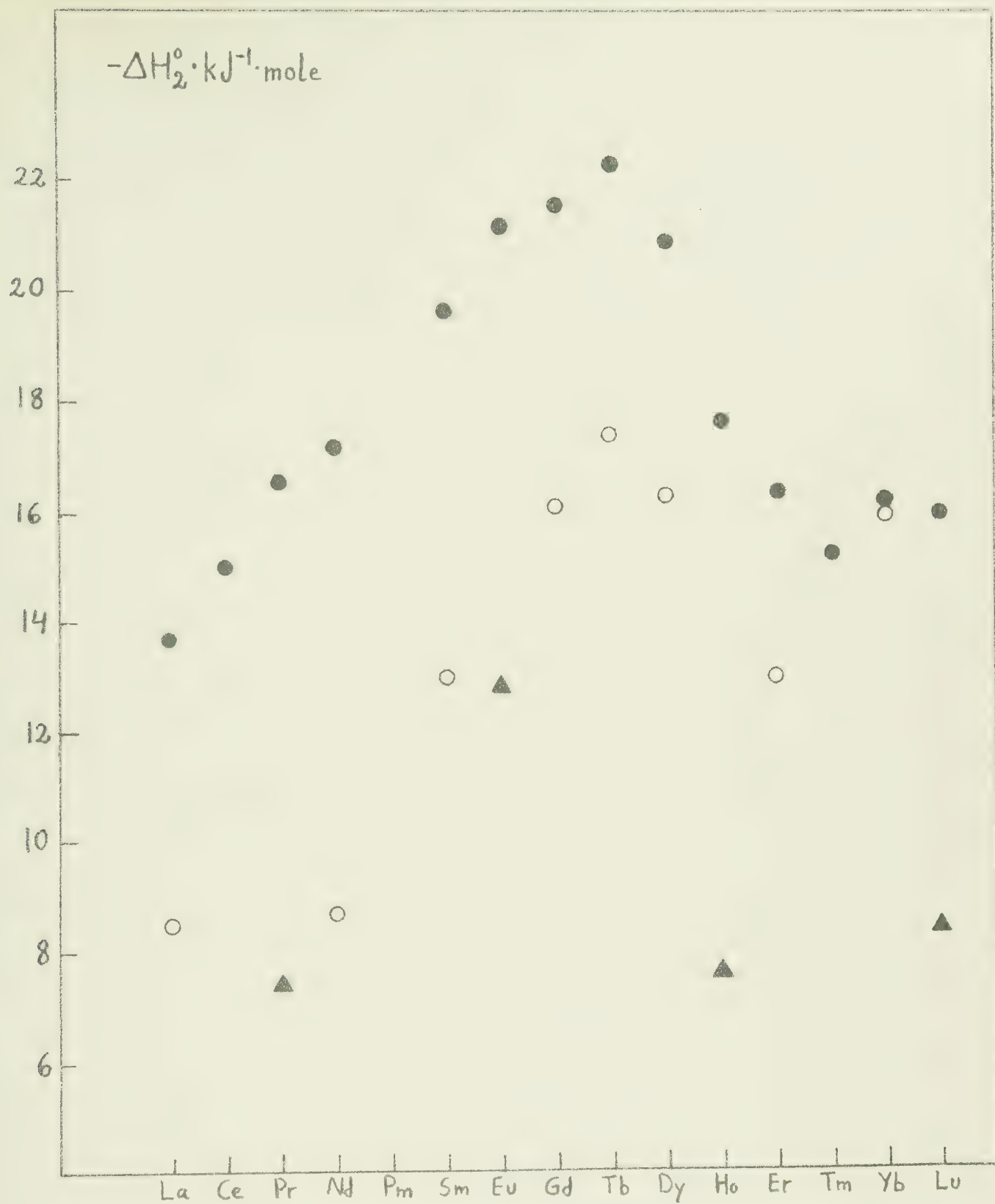


Fig. 4

● = dipicolinate, ○ = ethylenediaminediacetate,
▲ = iminodiacetate

